SERI/TP-211-3907 DE90000358 July 1990

Ion-Assisted Doping of II-VI Compounds During Physical Vapor Deposition

Final Subcontract Report 1 September 1985 - 30 August 1989

R.H. Bube, Principal Investigator Department of Materials Science and Engineering Stanford University Stanford, California

Prepared under Subcontract No. XB-5-05009-4





Solar Energy Research Institute

A Division of Midwest Research Institute

1617 Cole Boulevard Golden, Colorado 80401

Operated for the U.S. Department of Energy under Contract No. DE-AC02-83CH1009(SERI/TP-211-3907 UC Category: 273 DE90000358

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SERI Technical Monitor: C. Leboeuf

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Prepared for the U.S. Department of Energy Contract No. DE-AC02-83CH10093

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Printed in the United States of America Available from: National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161

> Price: Microfiche A01 Printed Copy A05

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IAD FINAL REPORT

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ABSTRACT

The purpose of this work is to investigate ion-assisted doping (IAD) during physical vapor deposition of CdTe and to determine the influence of co-deposition of ionized dopant atoms on the growth, structural, and photoelectronic properties of the deposited films. Results show that controlled doping in p-CdTe homo-epitaxial films up to $\approx 6 \times 10^{16}$ cm⁻³ for ion-assisted deposition with As ions and to $\approx 2 \times 10^{17}$ cm⁻³ for P ions has been achieved using ion energies of 30-80 eV. For a growth rate of $\approx 0.1 \ \mu\text{m/min}$, a substrate temperature of 400°C, and an ion energy of 60 eV, a maximum in doping density appears near an ion current of 0.6 μ A/cm², corresponding to $\approx 0.9\%$ of the impinging P ions being electrically active in the deposited film.

Related studies were also done, such as: (a) elucidation of the role of low energy ion damage in the ion-assisted doping process, and (b) investigation of the observed decrease in carrier density near the surface of p-CdTe on heating in a vacuum, H_2 , or Ar.

The ability to make carrier density profiles and to grade junctions is demonstrated. Preliminary results from polycrystalline p-CdTe films grown on graphite and alumina substrates are presented. Solar cells prepared using the epitaxial p-CdTe films as the collector material and n-CdS as the window are presented and the photovoltaic parameters are examined for different carrier densities and configurations in the p-CdTe. The solar cells provide a good diagnostic tool in studying the p-CdTe films grown by ion-assisted doping.

A summary of further research after the close of the contract period (the final part of Paul Sharp's Ph.D thesis research, from 9/23/89 to 5/10/90) is given in Appendix. I and a brief history of the program is in Appendix II.

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1. INTRODUCTION

1.1 Purpose for the Research

The primary problems for the utilization of polycrystalline (PX) p-CdTe based solar cells are those of obtaining sufficiently low series resistance (R_s) and of obtaining high open-circuit voltage (V_{oc}). The first of these problems has two aspects: (a) bulk, through-the-film resistance of the p-CdTe layer, and (b) contact resistance to the p-CdTe. Sufficiently increasing the p-type doping density in the CdTe would solve both of these aspects. Control of V_{oc} has been obtained by variation of the relative doping levels in the CdS and CdTe [1] for single-crystal based solar cells. Unfortunately this technique cannot be used at present for PX based cells because of the lack of control of p-CdTe doping. Thus control of p-type doping promises to be a tool for maximizing V_{oc} as well.

In the past we carried out a number of experiments designed to dope thin films of CdTe during deposition from the vapor phase, using closespaced vapor transport (CSVT) and hot-wall vacuum evaporation (HWVE). Successful doping of n-CdTe from the vapor phase with In was achieved using the HWVE process [2]. In neither the CSVT nor the HWVE approach, however, was there any indication of p-type doping of CdTe from the vapor phase, using such dopants as P, As, Cs, and Au. (The hole density in the p-CdTe layers *could* be increased within limit by increasing the substrate temperature during deposition, in a manner that is at least formally describable by a crystal defect model.)

Many of the dopants successfully used in bulk semiconductor growth present problems for film growth from the vapor due to low incorporation probabilities or surface segregation. However, impingement of low-energy dopant ions on the growing film during deposition can be used to significantly increase the sticking probability of the dopant species. The controlled use of this method of dopant incorporation, known as "lon Assisted Doping," (IAD) is becoming common in several thin film growth technologies [3]. The purpose of the work reported here is to investigate ion-assisted doping during the physical vapor deposition of CdTe. In particular the focus of the research is to determine the influence of the co-deposition of ionized dopant atoms on the growth, structural, and photoelectronic properties of the deposited films.

1.2 Doping of CdTe

1.2.1 Doping in single crystal growth

The carrier density in CdTe is controlled to a large extent by native defects, for material both with and without extrinsic impurities. For material without extrinsic doping, excess Te (low Cd pressure P_{Cd}) gives hole densities up to $\approx 10^{16}$ cm⁻³, by formation of acceptor-like Cd vacancies V_{Cd} and/or Te interstitials Te_i. Growth under higher P_{Cd} produces insulating material or, for still higher P_{Cd}, donor densities up to $\approx 10^{17}$ cm⁻³, due to Cd_i or V_{Te} [4].

Incorporation of rather high dopant densities is routine for bulk crystal growth of CdTe. By incorporating Group III elements In, AI, or Ga during crystal growth, high donor densities, up to 2×10^{18} cm⁻³ for In and Ga. can be obtained, depending on P_{Cd} [4]. For p-type doping, Group V elements, P or As, can be readily incorporated during crystal growth [5]. For example, P yields shallow acceptor densities up to 6 x 10^{17} cm⁻³ [6]. Bube et al. [7] report that addition of [P] = 2×10^{17} cm⁻³ to the melt for vertical Bridgman growth with excess Te results in a dopant electrical activity of nearly 100%; additional dopant does not increase the hole density but only reduces the electrical activity of the dopant. For single crystal (SX) growth with Sb and Bi there are few and conflicting reports, none of which suggest strong doping activity. Group I elements can provide shallow acceptor levels. Upon introduction during crystal growth, Na becomes substitutional and gives hole densities up to 2.5×10^{17} cm⁻³ [8]. Li can be introduced either during crystal growth or by subsequent diffusion, giving significantly higher carrier densities, up to $\approx 10^{19}$ cm⁻³ [8,9]. Unfortunately the stability of devices fabricated from p-CdTe:Li is measured in months at room temperature and hours or minutes at higher temperatures.

1.2.2 Doping in Thin Film Deposition

Carrier densities of $\approx 10^{17}$ cm⁻³ or larger are usually adequate to produce semi-ohmic contacts and minor series resistance losses on

single-crystal based cells. However, for polycrystalline (PX) materials the problems of doping are more severe because the oppositely charged grain boundary (GB) states effectively compensate the dopant; the free carrier density may be considerably less than the doping density. Doping levels well above $\approx 10^{17}$ cm⁻³ are required to reduce the grain boundary barrier heights sufficiently to obtain reasonable mobility values. In addition, the GB recombination velocity is smaller for lower GB potential barrier height indicating that higher solar cell efficiencies might be obtained with higher carrier densities [10]. It must be noted here that the difficulties in doping during film growth are also apparent when the films are grown epitaxially and thus contain no grain boundaries. Thus actual incorporation of the dopant into the film appears to be a large part of the difficulty.

Films of CdTe have been grown by a number of methods: vacuum evaporation [11], MBE [12], CSVT [13, 14, 15], electroplating [16, 16a], screenprinting [17], spray pyrolysis [17a], and chemical vapor deposition [18, 19]. However, obtaining sufficient carrier density in p-CdTe layers made by most film deposition techniques has been a persistent problem, as it also has been with some of the III-V materials and Si. Attempts at doping using Cu, P, Sb, As, and Na during deposition of CdTe by this group and others [11, 15, 18] have met with limited success and only marginal decreases in resistivity (or series resistance of devices) have been obtained. Maximum carrier densities in PX films have remained in the 5-10 x 10¹⁵ cm⁻³ range in most cases [20], even when such layers were grown epitaxially. Doping by metastable processes such as ion implantation [21, 22; As and P] or laser annealing [15, As] has been shown to produce substantially higher doping levels, but only for very thin layers of material. These latter methods could be used to deal with contact resistivity to a surface of CdTe already formed, but not bulk resistivity, Voc control, nor (conveniently) the doping of the CdTe layer adjacent to a substrate.

In the past few years there have been considerable advances in the introduction of dopants into CdTe thin films. T. Chu [18] reported the introduction of P or As (as PH₃ or AsH₃) during chemical vapor deposition (CVD) growth giving a p-type resistivity of 200 Ω -cm and carrier densities of $\approx 10^{16}$ cm⁻³, depending on close control of the CdTe stoichiometry. The PX films, on graphite substrates, were thick ($\approx 20 \ \mu$ m) and the grain sizes were large (20-80 μ m). Basol et al. [16], using electro-deposition were able to obtain p-CdTe polycrystalline films with 1 x 10¹⁷ cm³. Ghandhi et al. [19] used a chemically active

dopant, AsH₃, in MOCVD to obtain 2 x 10^{17} cm⁻³ in p-CdTe homoepitaxial films grown at a substrate temperature of 350°C. Using photon-assisted doping with As during MBE, Harper et al. [23, also see 12] were able to obtain 6 x 10^{18} cm⁻³ in p-CdTe homoepitaxial films.

Anthony et al. [13] using close-spaced vapor transport (CSVT), found no doping with P, As, Au, or Cs from single-crystal (SX) sources for PX growth on graphite or 7059 glass substrate and for homoepitaxial growth on SX CdTe. However, they obtained p-CdTe with $p \approx 10^{15}$ — 10^{16} cm⁻³ without extrinsic doping by control of the substrate temperature (up to 610°C) for CSVT growth. Tyan et al. [14] fabricated efficient PX p-CdTe-based cells by CSVT using a partial pressure of O₂ during the CdTe deposition. However, it is unclear whether *bona fide* doping was achieved.

Because of its ability to deposit films at near thermal equilibrium, hot-wall vacuum evaporation (HWVE) was thought to hold great promise for control of doping in CdTe. Indeed doping by co-evaporation of In vapor during HWVE growth of n-CdTe (Fig. 1) yielded maximum carrier densities of 2×10^{17} cm⁻³ for epitaxial growth on BaF₂ (essentially single crystal films) and 5×10^{15} cm⁻³ for PX films grown on 7059 glass under the same conditions [2]. The difference in carrier densities resulted from the compensating effect of grain boundary states in the PX films. Attempts at p-type doping were less successful. Huber and Fortmann [24] found no doping by As, Cu, Ag, Au, or Na by HWVE. Introduction of Sb during growth yielded either no change in carrier density or, at high Sb pressures, an abrupt change to high conductivity, suggesting metallic Sb precipitation. These workers found the same relation between carrier density and substrate temperature for undoped p-CdTe as did Anthony et al. [13].



Fig. 1. Dark and light resistivity of n-CdTe:In films grown on 7059 glass and on SX BaF₂, as a function of the In source temperature. Data points correspond to dark (•) and light (o) for films on glass, films on BaF₂ with $T_{sub} = 480^{\circ}C$ (Δ), and on BaF₂ with $T_{sub} = 450^{\circ}C$ (\Box).

Why then is it so difficult to dope CdTe p-type during film growth? The basic problem appears to be the incorporation of the dopant atoms into the growing film. First, most of the favored p-type dopants for CdTe (P, As, Na) have rather high vapor pressures so that the sticking coefficient for dopant atoms on the growing surface of the CdTe is very small at elevated substrate temperatures [e.g., 25]. Second, some of these dopants may suffer from strong surface segregation. A third aspect is the fact that many of the dopants evaporate in the form of molecular species (P4, As4, Sb2, etc.) that require high dissociation energies, on the order of several electron volts, to produce atomic species that can readily be incorporated into the growing film. Once the dopant has been incorporated into the growing film a further problem becomes evident. CdTe has a penchant for self compensation, in which the CdTe lattice responds to the introduction of a charged impurity by the creation of an oppositely charged native defect or complex, with the net result of no additional increase in hole density. Another, related difficulty is the amphoteric nature of some of the

dopants. For example, As commonly substitutes for Te to act as a shallow acceptor, but it can also substitute for Cd to form a triply charged donor As_{Cd} when the Cd pressure at the growth zone is insufficient [22, 26, 26a].

1.3 Description of the Ion-Assisted Doping Technique

1.3.1 Summary

Increasing the energy and chemical reactivity of component species by ionization during deposition is a much used technique for enhancing the structural and electronic characteristics of films [e.g., 1, 27]. More recently techniques for ionizing the major impinging constituents and/or dopants *during* growth by physical vapor deposition of semiconductors have been developed. The techniques have three major variations: (a) low dopant ion energy ($E_{ion} = 5$ to 100 eV) deposition, in which incorporation may be primarily by enhanced chemisorption [28, 29], (b) medium E_{ion} (50 to 800 eV) deposition in which implantation of the ions into the growing film plays an important part in their incorporation, and (c) ionized cluster beam deposition, in which the efflux from a Knudsen cell is expanded in the region of an ionizing electron beam, producing large clusters of constituent and dopant atoms which may or may not carry a charge [30, 31].

A figure of merit to evaluate the efficiency of the IAD process is the coefficient of incorporation C_i , defined as the ratio of the incorporated dopant atoms to total incident dose of dopant ions. C_i is a function of the sticking coefficient, impurity segregation at the growing surface, any ion implantion that may take place, and out-diffusion of already incorporated atoms. C_i sometimes includes the electrical activity of the incorporated dopant atoms as a factor; we use it here without factoring in the electrical activity.

To our knowledge our group at Stanford has been the first to apply ion assisted doping techniques to II-VI materials, despite the relative maturity of the technique.

1.3.2 Previous IAD work with Si and GaAs

In conventional MBE growth of GaAs and AlGaAs, several desirable ptype dopants cannot be used because of the low values of C_i (e.g., 10^{-7} for Zn). By using an incident beam of low energy (100 to 1000 eV) Zn ions, Naganuma et al. [29] and Matsunaga et al. [28] increased C_i by a factor of $\approx 10^5$ for Zn in GaAs. The crystal structure of the resulting epitaxial GaAs layers appeared to be as good as those of LPE and VPE p-GaAs layers. Because the value of C_i is approximately independent of ion energy for low ion energies, these authors felt that the primary mechanism for the increase of C_i is increased chemisorption. Bean and Dingle [32] used a similar technique with ion energies of 100 to 3000 eV, finding C_i values of up to 0.5 which depended only weakly on ion energy. They interpreted the dominant mechanism as simple ion burial rather than an electrostatic attraction between ions and surface atoms. They also found evidence of implantation damage which could be annealed out at higher temperatures.

Similarly Itoh et al. [33, Sb], Sigiura [34, Sb], and Ota [35, As] used IAD to greatly increase C₁ for Sb and As in MBE growth of Si layers.

In addition to increasing dopant incorporation, a prime advantage to the use of ion beams for doping is the ease and speed of their control. Dopant density can be regulated simply by changing the ion flux. An example is the technique for the growth of abrupt p/n junctions in Si by MBE using alternate beams of B and As is described by Swartz et al. [36].

1.3.3 Ion-assisted doping mechanisms

A complex variety of mechanisms come into play during ion assisted doping. These are illustrated in Fig. 2. The incoming flux consists of Cd atoms and Te₂ dimers with energies of fractions of electron volts and ions with energies in the 30 to 80 eV range. Momentum transfer from the incoming ions to the growing film is strongly affected by the presence of the lattice; an incoming ion transfers its momentum to the assemblage of atoms at the point of impact. In some respects this is like a rapidly decaying temperature pulse applied to a small portion of the lattice. The impact of the ions releases energy into the lattice which in some cases results in sputtering atoms from the surface. The ions can also undergo shallow ion implantation, on the order of 10 Å for our situation, as deduced from extrapolation of high energy ion implantation data. Ions can then re-evaporate from the surface, either directly or after diffusion from the interior of the growing film. Some are incorporated in the lattice in the proper substitutional sites, where they act as dopants, and some will find their way to improper sites where they may act as dopants of the opposite sign or be electrically inactive. There may be segregation of the dopant atoms at the growing surface, but this may be alleviated by collisional mixing when ions

strike the surface. Finally, if the dopant incorporation is sufficiently greater than the lattice can accommodate, then precipitation or, perhaps, compound formation can occur.

An additional complication for CdTe is the depletion of carriers observed near the surface on heating CdTe in various ambients, including vacuum, which is further described in Sect. 2.5. Suffice it to say here that at temperatures of $\approx 425^{\circ}$ C and above, Cd vacancies diffuse inward from the surface, whereupon P or As dopants move to the Cd sites (e.g., P_{Cd}) where they behave as donors, compensating the p-type doping. It is reasonable to assume that this also occurs during IAD growth, reducing the p-doping attainable. Since this mechanism depends on Cd vacancies, it would make the doping efficiency dependent on the micro-stoichiometry of the Cd and Te₂ vapor above the growing surface and of the surface itself.

Bajor and Greene [30] formulated a theoretical model for the incorporation of As into Si based on Ota's data [35], in which a balance was struck between low energy ion implantion, segregation at the surface, and out-diffusion to the surface with subsequent reevaporation of the dopant. A summary of the theory is given here to express the ideas involved. In the general case the incorporation rate for species i into the growing film is given by

$$I_{i} = J_{i}\phi_{i} + \xi_{i}\eta_{i} - \theta_{i} \left[\sum_{j} (\xi_{j} S_{ij}) \right]$$
(1)

where J and ξ are the fluxes of thermal and accelerated species *i*, ϕ is the sticking probability of thermal species, η is the trapping probability of accelerated species, θ is the surface fraction of the species, and S_{ij} is the sputtering probability of species *i* by species *j*. In Ota's experiments a bend in the ion path was used to trap the neutral flux so J_{As} = 0 and the surface temperature was high enough so that $\theta_{As} \approx 0$, and Eq. (1) reduces to

$$I_{As} = \xi_{As} \eta_{As} = C_b R = \xi_{As} C_{i,As}$$
⁽²⁾

where C_b is the As concentration far from the surface (steady state), R is the growth rate of the film, and $C_{i,As}$ is the incorporation probability. The As depth profile for the growing film is given by the solution to Fick's second law:

$$\partial C_{AS}(x,t)/\partial t = \partial F_{AS}(x,t)/\partial x$$
 (3)

12



Fig. 2. Mechanisms taking place in ion-assisted deposition. "Other Effects" include (a) near-surface doping compensation on heat treatment (see Sect. 2.5), (b) ion damage (see Sect. 2.4), and (c) annealing out of ion damage at elevated temperatures.

Here $C_{AS}(x,t)$ is the concentration and $F_{AS}(x,t)$ is the net flux of As given by:

$$F_{AS}(x) = F_{I}(x) + F_{D}(x) + F_{S}(x)$$
 (4)

where $F_I(x)$, $F_D(x)$, and $F_S(x)$ are the flux components due to implantation, diffusion, and segregation, respectively. Eq. 3 is transformed using a moving coordinate system in which x' = x + Rt and solved giving

$$C_{AS}(x') = F_{AS}(x')/R + C_{b}.$$
 (5)

The flux due to implantation given by:

$$F_{I}(x') = \xi_{As} \frac{\int_{x'}^{\infty} f(x')dx'}{\int_{0}^{\infty} f(x')dx'}$$
(6)

where f(x') is the distribution function which describes the implantation profile and includes the ion range (a function of ion energy) and the straggle. The second term on the right of Eq. (3), $F_D(x')$, describes diffusion toward the surface and is given by

$$F_D(x') = -D_{AS} [dC(x')/dx'].$$
 (7)

The diffusion coefficient D_{As} is modified in the near-surface region to account for the enhancement due to ledges, kinks, and random nuclei by the following equation:

$$D^{*}(x') = D_{AS} [1 + B \exp(-x'/I_D)],$$
 (8)

where B is a temperature dependent constant and I_D is a characteristic length on the order of 1 nm. The final term of Eq. (3), $F_S(x')$, expresses the segregation of As near the surface due to strain free energy (As is larger than Si on the lattice) and the decrease in surface free energy when As replaces some of the Si atoms on the surface:

$$F_{S}(x') = \{ D_{As} \Delta G^{\circ}_{seg} C_{As}(x') / | k T \} \exp(-x'/l), \qquad (9)$$

where ΔG°_{seg} is the Gibbs free energy of segregation and I is the characteristic length of the segregation potential. Making the appropriate substitutions gives relations describing the profile of the As concentration and the incorporation probability as a function of ion energy and temperature. The three unknown constants I, I_D, and B are determined from physical constraints and by fitting an experimental data set.

To modify this theory to describe our case it would be necessary to incorporate terms describing (a) the flux of P or As neutrals to the CdTe surface, (b) the additional loss of carriers due to self compensation (desc. above and Sect 2.5), and (c) possible collisional mixing. However, CdTe is not as well characterized as Si and many of the physical constants have not yet been measured.

Rockett et al. [37] have reported increases in the incorporation of In of over four orders of magnitude using 100 eV In+ ions in MBE Si. These experimental results were explained by a model developed by Greene et al. [38, 39] which accounted for both trapping (i.e. low-energy implantation) and the effect of implantation on surface segregation kinetics. According to this model the use of accelerated In+ doping decreased the amount of surface segregation due to the fact that a fraction of the ions are implanted at depths which are of the order of the spatial extent of the surface segregation potential. The decreased segregation rate resulted in a decrease in the steady state In coverage, and hence in lower desorption rates and higher incorporation probabilities. Similarly, the decreased segregation rate also resulted in less dopant profile broadening.

2. EXPERIMENTAL WORK

2.1 Deposition System

Our apparatus consists of an ion source, a movable Faraday cup for monitoring ion current, an effusion cell for CdTe, and a heated substrate holder, all situated in a vacuum system with a base pressure of $\approx 6 \times 10^{-8}$ Torr during deposition, as shown in Fig. 3. The ion source design, which follows that of Rockett, Barnett, and Greene [40], uses a boron nitride Knudsen cell to supply the dopant atoms and an ionizer section with a tungsten filament and a graphite anode and an extraction grid (Fig. 4). Arsenic was tried first as a dopant because of reports of metastable doping using As [41] and because of its vapor pressure. Typical CdTe growth rates are 1-20 μ m/hr, and As ion currents as high as 100 μ A/cm² at the substrate have been obtained, corresponding to a doping level of 2 x 10²¹ cm⁻³, assuming C_i = 1 and that all the As atoms are electrically active.



2.1.1 Characteristics of the ion gun

Plots of the ion current, measured with a Faraday cup, and anode current versus As effusion cell temperature are shown in Fig. 5. As the pressure of As becomes larger with increased cell temperature the space charge around the filament is neutralized by the increasing density of positive ions, so the anode current (electrons) increases to a plateau where it is limited by the number of electrons emitted by the filament.



Fig. 4. Ion source. For As, the effusion cell typically operates at 230°C.



Fig. 5. lon current and anode current as a function of As effusion cell temperature. Anode voltage = 50 V and grid voltage = 400 V.

The ion current density plotted against extraction grid voltage in Fig. 6 shows a saturation above about 500 V.



Fig. 6. Ion current density vs. extraction grid voltage for As cell. The As cell temperature is 380° C, anode current 1.25 A, and Faraday cup voltage = 200 V.

Figure 7 shows the anode current and ion current plotted against anode voltage. Increasing anode voltage overcomes the space-charge limitation on the anode current, thus increasing the efficiency of ionization and the ion current.

Estimates of ion current vs position show the beam to be quite strongly focused with an area of maximum current density about 1.5 cm in diameter and to fall off approximately as $1/r^2$, where r is the distance between the source and the Faraday cup used to measure beam current. Films of As were grown on glass at room temperature without ionization to check the operation and to evaluate the ion-to-neutral ratio. Auger analysis of one of these films shows a pure As signal.



Fig. 7. Ion current and anode current vs anode voltage for As source temperature 380° C and grid voltage = 200 V.

2.1.2 Initial experiments

In order to check the flux and incorporation of the dopant several experiments were done. For example, As ions (with no CdTe flux) were impinged onto SX CdTe substrates using an ion current density of 50 μ A/cm² at the substrate, an ion energy of 400 eV, and a substrate temperature of 350°C. Auger results show approximately 20 Å of material with an As dose of about 10²¹ cm⁻³, the As density dropping to zero after about 40 Å (Fig. 8). The As penetration into the single crystal CdTe is of the order of magnitude predicted by extrapolation of ion implantation data to these low energies. Microscope examination revealed that the ion beam had sputtered away about 0.4 μ m of CdTe during the 30 min deposition time. The Auger results demonstrate that As is indeed present in the CdTe SX, despite removal of the CdTe by As ion sputtering during the deposition.



Fig. 8. Auger signals for As ion impinged CdTe SX (with no CdTe flux). Top: surface. Bottom: about 23 Å sputtered away in the Auger. At 46 Å no As was detectable.

Comparison of the As layers resulting from ion deposition on 7059 and ITO coated 7059 suggests that substrate charging may be important for insulating substrates. As ions (with no CdTe flux) were deposited onto ITO/7059 using a substrate temperature $T_{sub} = 350^{\circ}$ C, an ion current density of 50 μ A/cm², and an ion voltage of 400 V. Auger results on these samples show that As diffuses into the bulk ITO to large distances (corresponding to 33 min Auger sputtering time).

In another experiment, a CdTe film was grown on a graphite substrate at 350°C with a simultaneous flux of 100 μ A/cm² (at the substrate) of As at 200 eV. SIMS measurements at SERI showed that $\approx 10^{20}$ cm⁻³ of As was incorporated into the film.

2.2 Experimental Technique

2.2.1 Substrate preparation and film deposition techniques In order to clearly show that ionized p-type dopants could be incorporated into the crystalline structure and to avoid problems associated with grain boundaries mentioned earlier, at first we grew thin films on single-crystal CdTe [42]. The CdTe boules contained grains up to ≈ 2 cm in diameter. The boules were oriented with the help of Laue patterns and the substrates were cut 4 x 12 x 2 mm³. Results indicated that good epitaxial films could be obtained independent of orientation. However, the film growth rate did depend strongly on the orientation and for any series of experiments the orientation was kept constant. Some of the substrates had twins and smaller grains of other orientations.

In most cases the substrate material was p-CdTe:P, grown with excess Te during the first growth, and then doped with Cd₂P₃ to $\approx 2 \times 10^{17}$ cm⁻³ prior to the second growth [42]. The material was grown by the Bridgman technique with 60 Hz vibration on the vitreous carbon lined quartz ampoule during crystallization. The electrical activity of the dopant was nearly 100% for this method of growth. In some cases a n-CdTe:In, grown by II-VI, Inc., with an estimated resistivity of >10³ Ω was used.

The substrates were lapped on 600 grit SiC wheels using water as a lubricant, then chem-mechanically polished [43] with a 1.5% bromine-polyethylene glycol solution, removing about 100 μ m of material. Immediately prior to film growth the substrates were ultrasonically cleaned in trichloroethane for 90 seconds, etched 5 minutes in a 3% bromine-methanol solution (removing about 50 μ m of material), rinsed with methanol, and blown dry with dry nitrogen.

In some cases, particularly for the early part of the work, the substrates were thermally etched at 425°C in H₂ for 5 min immediately after the MeOH-Br etch, then promptly put in the system for deposition. This step was done to eliminate the Te rich surface layer left by the MeOH-Br etch and thus provide a stoichiometric surface [44]. In later work the H₂ anneal was replaced by holding the sample at temperature in the vacuum system prior to deposition. There was no apparent difference in the effects of these two methods.

A substrate was then loaded into the substrate holder. The substrate holder screws were tightened, bringing the substrate into contact with $Electrodag^{TM}$ coated AI foil that was, in turn, in contact with a resistance heated plate. A thermocouple was pressed down through the heated plate onto the AI foil. Usually, a single substrate was used for each run. When the conditions for growth were achieved, the shutter was opened to commence film growth.

Elemental As or P was used in the ion source and the ion current was monitored with the Faraday cup before each deposition. Usually one half of each substrate was covered during the deposition to act as a control. Deposition was done at substrate temperatures T_{sub} of 350 to 500°C, film thickness varied from 5 to15 μ m, and the time at T_{sub} in vacuum was 30 to 60 min. After deposition, In Schottky barrier contacts were applied to the film and the covered portion of the substrates (two on each), and Au semi-ohmic contacts were applied to the p-CdTe substrate, all by vacuum evaporation.

Most of the films grown on the SX substrates were epitaxial, following the orientation of the substrate. The substrates usually contained two or three differently oriented grains. On some grains the morphology of the films was completely smooth under 200x Nomarski examination, suggesting single crystallinity. On other grains with different orientations however, the surface morphology showed oriented growth features (such as escarpments), suggesting film grains with minor misorientation (Fig. 9).

2.2.2 Photoelectronic measurement techniques

Current-voltage characteristics of each of the four In diodes were measured, using an automated measuring system, using an HP 310 computer, a Keithley 619 dual electrometer, and a Keithley 230 programmable power supply. The three-point measuring technique [50] was used to eliminate the contact resistance of the back, semi-ohmic contact to the p-CdTe substrate. The diodes were generally measured in a cycle from 0 V to -7 V reverse bias, then back to +2 V forward bias at a data collection rate of \approx 1 point/sec. For reverse bias hysteresis was almost always observed, suggesting the presence of deep traps (see Fig. 17b and c). The data were reduced to yield J₀ and the A factor for each diode. The high forward-bias roll-off was used to get the value of the series resistance of the diode R_s, which served as an indication of the through-the-film resistivity of the IAD layers.



Fig. 9. Microphotograph of two samples showing growth on several differently oriented substrate grains. Left: #19 As-1-SX, $J_{ion} = 2 \mu A/cm^2$, $T_{sub} = 400$ °C. Right: #26-As-2-SX, $J_{ion} = 1.5 \mu A/cm^2$, $T_{sub} = 300$ °C. Both at 30 eV ion energy. Magnification 200x. Lamellar twins are not visible on polished substrate but greatly influence growth morphology and rate.

Carrier densities in the resulting films were measured using Mott-Schottky plots of $1/C^2$ vs V data taken at 1 or 2 MHz by an automated HP 4275A LCR meter for the In M/S diodes. In some cases a gradient appeared in the carrier density (p) vs depletion layer width plots derived from the $1/C^2$ vs V data. This gradient in can either be a real gradient of p in the sample or an artifact resulting from the presence of deep states in the depletion layer [45]. The two cases could most easily be distinguished by etching off a thin layer and remeasuring the $1/C^2$ vs V data; if the gradient reappeared with negligible change in shape and magnitude, then the apparent gradient was due to deep states.

Other, specific measurement techniques are described where pertinent in the following sections.

2.3 Doping Experiments With Single-Crystal Substrates

2.3.1 Doping as a function of ion current, ion energy, and substrate temperature

Schottky diodes of In were evaporated onto the films and plots of carrier density versus depletion layer width (Fig. 10) were calculated from the slope of the $1/C^2$ vs V data for the diodes. These plots showed some anomalous structure and hysteresis at larger reverse bias voltages, suggesting the presence of large densities of electrically active deep states [e.g., 45]. The gradient in p for the no ion case and the substrate in Fig. 10 probably arises from the surface decrease in hole density due to heating, described in Sect. 2.5. The growth with no ions gave a hole density of $\approx 10^{14}$ cm⁻³, a value typical of other growths with no ions. Increasing As ion current gave increasing hole density, up to 2-3 x 10^{16} cm⁻³ for these growth parameters.



Fig. 10. Carrier density vs depletion layer width for selected IAD samples. All the ion doped samples were grown at $V_{iOI} = 30 \text{ eV}$ and all the films were grown at $T_{SUD} = 400^{\circ}$ C. Ion current density is indicated on the curves. "Substrate" indicates data for a diode on a portion of the substrate covered during deposition.

The zero bias value of the measured carrier density is plotted versus As ion current density in Fig. 11. The carrier density rises smoothly as a function of ion current density J_{ion} , reaching a maximum at \approx 1.3 μ A/cm². This value of ion current corresponds to an As density in the film of N_i = J_{ion}/q G = 4 x 10¹⁹ cm⁻³, if all of the impinging As were incorporated, where q is the electronic charge and G is the film growth rate.



Fig. 11. Measured hole density vs. J_{iOn} for As ions. All data is for $T_{Sub} = 400^{\circ}C$ and $V_{iOn} = 30$ V. Growth rate is 6-9 μ m/hr.

The carrier density for films grown without ion flux, under the same conditions, was $\approx 10^{14}$ cm⁻³.

Carrier density, plotted against ion energy in Fig. 12, shows a shallow maximum around 50-80 eV and then drops for energies greater than 100 eV. The drop may be due to ion damage, discussed in Sect. 2.4.

The effect of variation of T_{sub} , shown in Fig. 13, shows considerably reduced doping at high T_{sub} and suggests either out-diffusion of the dopant or in-diffusion of a compensating defect, discussed in Sect. 2.5 and/or increased re-evaporation of the dopant at higher T_{sub} .







Fig. 13. Hole density vs. substrate temperature for As ions with V_{ion} = 30 V and J_{ion} \approx 1.5 μ A/cm².

Similar results were obtained for P ions. A plot of hole density vs N_{ion} for two rates of film deposition are shown in Figs. 14 and 15. The maximum for P ions appears to be somewhat sharper than for As ions and the ion flux at the maximum for P appears to be slightly lower than for As ions. For the lower deposition rate the maximum is shifted toward higher N_{ion} values than for the higher rate, suggesting that more P atoms re-evaporate before they are buried at the slower rate.



Fig. 14. Measured carrier density vs. P ion density for films deposited at \approx 7 μ m/hr.

A data set taken later in the contract period is shown in Fig. 15A. The data are grouped more closely due to tight control of T_{sub} , filling of the CdTe effusion cell, and crystallographic orientation of the substrate. This curve shows a broadened maximum, compared to Figs. 14 and 15.

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To determine whether the observed doping was *bona fide*, substitutional doping with the ion species, or just an effect of ion damage, a number of runs were done using Ar ions, rather than As. For small to moderate J_{ion} , the p values for these films were quite similar to those with no ion flux (one of which is shown in Fig. 10). For larger J_{ion} , capacitance results showed that the entire film (\approx 10 µm) was either depleted or inverted. Thus, the doping observed in the experiments must be due to the incorporation of dopant in the film as a result of the impingement of dopant ions.

One of the advantages of IAD is the control of doping by simply changing J_{ion} . An example of this is shown by the stepped doping profile in Fig. 16, for which J_{ion} was decreased stepwise as film growth proceeded. Since the steps in J_{ion} are abrupt (film growth was stopped temporarily when J_{ion} was changed), the data show interdiffusion of the order of \approx 300 Å. The ability to grade or step the doping is useful in fabricating various kinds of devices with built-in carrier density profiles.



Fig. 15A. Measured carrier density vs. P ion density for films deposited at \approx 10 μ m/hr, with T_{sub} = 400°C and V_{ion} = 60 V.

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Fig. 16. Carrier density as a function of depth in a staircase doped film, obtained from $1/C^2$ vs V data.

To determine the amount of dopant actually incorporated in the film SIMS measurements of P density in a film were done at SERI [45a], using a single-crystal sample of p-CdTe:P grown by the Bridgman technique as a standard. The amount of P put into the growth ampoule for the single crystal standard closely corresponded to the measured carrier density of $\approx 2 \times 10^{17}$ cm⁻³. In one case, for sample SC-35, the P density in the film was found to be $\approx 4 \times 10^{17}$ cm⁻³, whereas the measured carrier density in the film was $\approx 2 \times 10^{17}$ cm⁻³. Thus, since the film was grown with J_{ion} = 0.47 μ A/cm² and the growth rate was 7.5 μ m/hr (giving N_i $\approx 1.4 \times 10^{19}$ cm⁻³) about 97% of the P was rejected at the surface, and about half of the P incorporated was electrically active.

2.3.2 In/CdTe diode characteristics on IAD films Typical log J vs V characteristics for In diodes on IAD doped films are shown in Fig. 17.



Fig. 17. Forward and reverse log current density vs. applied bias for several P doped samples: (a, top) single crystal with no heat-treatment, $p \approx 2.5 \times 10^{16} \text{ cm}^{-3}$ (also SIMS standard); (b, middle) IAD film, (sample FR-5-1), grown at $T_{Sub} = 400^{\circ}$ C, with $J_{ion} \approx 0.07 \ \mu\text{A/cm}^2$ and $V_{ion} = 60 \text{ V}$; and (c, bottom) IAD film, (sample FR-9-2), grown at $T_{Sub} = 400^{\circ}$ C, with $J_{ion} \approx 1.1 \ \mu\text{A/cm}^2$ and $V_{ion} = 60 \text{ V}$ (Signs are changed for reverse bias branch.)
In general, the films with low to moderate ion doses and ion energies $\leq 100 \text{ eV}$, as well as the adjoining substrates showed forward-bias log J vs V characteristics that could be described well using two exponential branches and series and parallel resistances:

$$J = J_{01}[exp(qV'/A_1kT) - 1] + J_{02}[exp(qV'/A_2kT) - 1] + V'/R_p$$
, and

$$V' = V - JR_s$$
.

Comparison of In/p-CdTe diode current vs voltage data for these films and the adjoining substrates showed similar values of the parameters: $J_{01} \approx 0.3 \times 10^{-8} \text{ A/cm}^2$, $A_1 = 1.8$ to 2.3, $J_{02} = 0.4$ to $4 \times 10^{-12} \text{ A/cm}^2$, and $A_2 = 1.0$. These values are typical for In Schottky barriers on SX p-CdTe which are dominated by thermionic emission at higher voltages and recombination/generation in the depletion region for lower bias voltages (Fig. 17a).

For films deposited at the highest J_{ion} and/or the highest V_{ion} , the current-voltage data could be described well by a power law:

 $J = J_{00}V^{n} + V/R_{p}$, where 2 < n < 2.5,

· . .

suggesting transport by space-charge-limited current through an effectively insulating layer of semiconductor.

In general the IAD samples showed reverse-bias currents $J_r(V)$ similar in form to those for the substrate controls, but larger in magnitude (Fig. 17b, c). The magnitude of J_r increased with increasing ion dose. The shape of the J_r (at fixed reverse bias) versus J_{ion} curve is roughly the same as that of the carrier density p vs J_{ion} , indicating an approximate proportionality between J_r and p. The value of throughthe-film series resistance, which includes the bulk resistance of the substrate and the film and the contact resistance, determined from the high forward-bias roll off of the log J-V curves, decreased with increasing J_{ion} .

The reverse J-V curves for In diodes on the IAD films showed a "figure 8" hysteresis in reverse bias as the bias went from 0 V to -7 V and back to 0 V at a rate of approximately 0.2 V/sec. Generally, the hysteresis appeared to increase somewhat with the ion dose. This is

indicative of deep states for which the state of charge influences the junction transport.

2.4 Ion Damage Experiments

2.4.1 Overview

The data of Fig. 12 suggest that the decrease in hole density for higher ion energies might be caused by ion damage. To elucidate this, a separate study of ion damage effects on p-CdTe was initiated. The effects of low-energy Ar ions (0-800 eV), both from the ion beam and in an rf sputtering unit, on the surface of SX p-CdTe were investigated as a function of the ion energy, using measurements of J vs. V, quantum efficiency, and $1/C^2$ vs V for In junctions on the CdTe. A threshold for the effects was identified at an accelerating voltage of slightly less than 100 V for a fluence of 5 x 10⁻³ C cm⁻². Bombardment by Ar ions at voltages larger than this results in the formation of an n-type surface layer on the p-CdTe crystals.

2.4.2 Ion damage results and discussion

Type conversion of the surface of CdTe crystals with processing has been frequently observed. For instance, the conversion of the surface layer of p-CdTe single crystals to n-type by ion bombardment has been reported by Courreges et al. [46], who observed the effect as a result of sputter deposition of indium tin oxide on p-CdTe single crystals at sputtering voltages between 0.8 and 1.6 kV. Similar effects were reported by Tsai et al. [47] for the sputter deposition of indium tin oxide on p-InP single crystals at 2.5 kV. Type conversion from n-type to p-CdTe with processing has also been described by Bodakov et al. [48] and Basol et al. [49].

The p-CdTe crystals used in this work were grown and prepared as outlined in Sect. 2.2.1 with the following exceptions. The hole density was 8 x 10^{16} cm⁻³. The wafer surface for these experiments was parallel to the (111) plane. This orientation was selected because (a) an open channel appears along the [111] direction, thereby enhancing ion-implantation effects, and (b) thin-film CdTe deposited on amorphous substrates shows a preferred [111] orientation in most cases.

Semi-ohmic contacts to the rear of the p-CdTe were made by the deposition of Au stripes on a surface etched with $K_2Cr_2O_7$: H_2SO_4 : H_2O and rinsed with DI water and methanol. All current-voltage

measurements were made using a three-point technique [50] to eliminate the effects of contact resistance at this back contact.

CdTe substrates were bombarded in the IAD system for 3 min with an Ar ion beam at RT using voltages from 0 to 400 V and with an ion current density of 28 μ A/cm² at the substrate as measured by the Faraday cup. An In contact was evaporated onto the bombarded surface with minimum exposure of the sample to air between bombardment and In evaporation. Current-voltage data for the resulting junction shown in Fig. 18. The ion-damaged samples show an increase in current, particularly for low bias voltages. The sample exposed to ions with energy of 100 eV shows a log J vs V curve similar to that of the control, but with higher currents at all voltages, suggesting that the threshold for damage is slightly less than 100 eV for this case.

This conclusion is consistent with the quantum efficiency curves for the ion-damaged samples, shown in Fig. 19. In the experimental situation used, with an opaque In contact on the surface, lightgenerated current is collected around the circumference of the dot, and the magnitude of the response depends on the conductivity type of the surface and the effective distance x_c from the edge of the In contact over which photoexcited carriers can be collected. If the surface is ptype, then it is expected that this effective distance is approximately the diffusion length of electrons plus the depletion layer width. If the surface is converted to n-type, however, the junction becomes a homojunction, the In becomes an ohmic contact to the n-type surface layer, and the effective distance of collection is limited only by the resistance of the n-type layer (and the total area converted to n-type if the resistance is sufficiently small). Exposure to ions with 100 eV energy definitely has less effect than ions at 200 or 400 eV, but also marks the clear beginning of changes in the p-CdTe surface.

Quantum efficiency is defined by $\eta_Q = I_{sc}/q\Gamma A$ and in this case the collection area is $A \approx 2\pi Rx_c$, where R is the radius of the In dot, I_{sc} is the short-circuit current, q is the electronic charge, Γ is the photon flux (cm⁻² s⁻¹), x_c is the effective collection distance from the edge of the In dot, and η_Q is the actual quantum efficiency. Thus, the vertical axes of Fig. 19 and 21 are a plot of $I_{sc}/(2\pi RqF) = x_c \eta_Q$. The "quantum efficiencies" of Figs. 19 and 21 (η_Q ') have been normalized only by $2\pi R$; to fully normalize them with respect to area we must divide them by the collection distance x_c . We can obtain an approximation for x_c by

assuming that the fully normalized quantum efficiencies have a plateau at $\eta_Q \approx 0.7$. Thus $x_c = \eta_Q'/0.7$.

<u>Ion Energy (eV)</u>	n <u>o' plateau (cm)</u>	<u>x_c (μm)</u>	
0	2.70 x 10 ⁻⁵	0.4	
100	1.15 x 10 ⁻³	16	
200	1.20 x 10 ⁻²	171	
400	1.50 x 10-2	214	

The collection length data can then be analyzed by the following. The light-generated carrier collection to a grid line on the front of a solar cell with a thin front layer is given for one dimension by [50, p. 225]

$$d^2 V/dx^2 = J(V)\rho/t, \tag{1}$$

where J(V) is the current-voltage characteristic of the solar cell and t



Fig. 18. J vs V dependence for In junctions on an Ar ion-damaged p-CdTe surface.



Fig. 19. Quantum efficiency of In junctions on an Ar ion-damaged p-CdTe surface.

and ρ are the thickness and resistivity of the film through which the carriers are collected. For the small current densities typical of a quantum efficiency measurement, J(V) can be approximated by

$$J(V) = -J_{sc}(1 - V/V_{oc}),$$
 (2)

where V is the applied bias and V_{oc} is the open-circuit voltage. The solution to Eq. (1) is

$$V(x) = V_{oc} \{1 - exp[-(J_{sc}\rho/V_{oc}t)^{0.5} x]\}.$$
 (3)

We can quantify the collection length x_c as the distance from the edge of the In contact for which the current density is reduced to 1/e of its value at the contact by the voltage drop in the resistive layer. For values of x_c much larger than the minority carrier diffusion length L_d we can neglect L_d . Now using Eq. (2), at x_c we have

$$J(V)/J_{sc} = 1/e = (1 - V/V_{oc}) = exp[-(J_{sc}\rho/V_{oc}t)^{0.5} x_{c}]$$

so that

$$x_{c}^{2} = V_{oc}t/J_{sc}\rho = (x_{ro}V_{ion}^{0.8}) V_{oc}/J_{sc}\rho,$$
 (4)

Here we have approximated the thickness t of the type-converted layer by the range of the ions in the CdTe:

$$t \approx x_{ro} V_{ion}^{0.8}$$
 (5)

where x_{ro} is the range constant and the relation is assumed to be the same as that for P in Si [50a]. Thus a plot of $x_c^{2.5}$ versus V_{ion} should yield a straight line. Comparison of this theory to experimental data in Fig. 20 suggests that there is a threshold for the type conversion at ion energies of about 100 eV and that below that either Eq. (5) doesn't hold or that the ion damage is unable to produce type conversion.



Fig. 20. (Collection length)^{2.5} versus ion voltage for the samples damaged by the ion beam.

CdTe substrates were also sputter damaged with Ar at voltages up to 800 V for 3 min each in a Perkin-Elmer rf sputtering unit [51], with half of each substrate covered by a high-purity graphite sheet, to act

as a control. To ignite the plasma, a high voltage (>1000 V) is applied and then quickly decreased to the desired value for sputtering. Although this initial high-voltage plasma bombardment was of only 1-2 s duration, it dramatically affected the surface of the CdTe.

After rf sputter damage, indium contacts were evaporated on both the sputtered and un-sputtered surfaces with minimum exposure to air. The variation of current with bias voltage for the diodes on these samples shows that exposure of the surface to only the plasma ignition before junction formation produces a major change in the junction properties. Subsequent sputter damage decreases the current at higher voltages and increases the current at lower bias voltages with increasing ion energy.

The results of $1/C^2$ vs V measurements on these junctions, using the automated HP 4275A LCR meter and plotted as carrier density vs. depletion layer width, show that the data for the control samples are almost identical to those for the sample exposed to the plasma ignition only (without extended sputter damage). For samples sputter damaged at 600 and 800 V, however, major decreases in carrier density are observed, from 4 x 10¹⁶ cm⁻³ without sputter damage to 2 x 10¹⁵ cm⁻³ with sputter damage, with a large increase in the depletion-layer width. This result is consistent with conversion of the surface of the crystal to n-type with sputter damage, the resulting depletion-layer width then being the sum of the n- and p-type depletion layer widths.

The quantum efficiency of these junctions, shown in Fig. 21, indicates a much larger response for all of the samples compared to the controls, a result consistent with the conversion of the surface of the p-CdTe to n-type by exposure to the plasma ignition alone, as well as to any additional sputter damage. It is also observed that the magnitude of the quantum efficiency for the sputter-damaged samples is independent of the size of the In contact (not the case for the control sample). If a genuine homojunction were formed with an appreciable n-layer thickness, then it would be expected that the response would decrease toward shorter wavelengths because of the recombination loss at the front n-type surface; indeed the data for the sample damaged at 600 V begin to show this behavior and it is well defined for the 800 V sample data.



Fig. 21. Quantum efficiency of junctions formed on sputter damaged p-CdTe surfaces. "Unbombarded was control sample. All other samples were exposed to the plasma ignition.

If the quantum efficiencies of ion-beam-damaged samples are compared with that for a sample damaged only by the plasma ignition in the sputtering chamber, it appears that the damage caused by a few seconds of plasma ignition is equivalent to 3 min of ion-beam bombardment at 200 V. Thus, for a sputter damage below 200 V, the initial plasma ignition appears to be the dominant part of the sputter damage process. If the magnitudes of the quantum efficiency for samples subjected to 3 min of ion-beam damage at 200 and 400 V are compared to those for samples subjected to sputter damage at 200 and 400 V after exposure to the plasma ignition, it is found that the quantum efficiency of the latter is about four times larger than that of the former, indicating the greater degree of surface damage and type conversion sustained in the sputtering apparatus.

These results demonstrate the potential problems associated with using conventional rf sputtering and/or ion beam techniques for fabrication of CdTe-based devices.

2.5 Effects of Heat Treatment on the Near-Surface Carrier Density in p-CdTe

2.5.1 Introduction

The thermal etch in H₂ given to many of our p-CdTe substrates before deposition causes the formation of a 0.2 to 0.5 μ m surface layer with substantially lower carrier density than the bulk material. This effect occurs on heating in vacuum as well and can be expected to influence the carrier density in the growing films for IAD deposition.

The purpose of this phase of the work is to investigate the mechanism in which the carrier density of p-CdTe:P decreases due to heat treatment. By successive etching of a heat-treated sample, the carrier density profile resulting from carrier loss near the surface was found to be a real effect rather than an artifact of measurement. Further experiments with varying Cd and P vapor pressures indicate that compensation occurs through the formation of P_{Cd} anti-site donors. Observation of the reverse reaction by annealing a sample of p-CdTe:P with CdTe powder after first annealing in vacuum shows that it does occur but at a much slower rate than the formation of the P_{Cd} defects.

2.5.2 Background

In the process of fabricating solar cells and other devices, CdTe is usually exposed to certain heat-treatments (such as annealing in H₂ at 425° C for 5 min) to improve its surface properties [44]. As a byproduct of these heat treatments, a decrease in carrier concentration near the surface has been observed. This phenomenon is common to both n- and p-CdTe annealed in various ambient conditions such as in H₂, N₂, Ar, and vacuum [44, 52-58]. Similar effects have also been observed in some as-grown p-CdTe thin films [59, 60].

It is generally thought that for n-CdTe, this effect is caused by the creation and in-diffusion of Cd vacancies (V_{Cd}) at the surface due to different rates of evaporation of Cd and Te from CdTe [56, 58]. As an acceptor species when ionized, V_{Cd} can compensate the donor impurities present in the material. This explanation seems to be consistent with the results obtained from annealing undoped CdTe (slightly p-type) in which the hole concentration increases near the surface [61, 62]. However, a loss in carrier density is also observed in more heavily doped p-CdTe:P [44, 52, 53], and the model does not fit since it predicts an increase rather than a decrease in carrier density.

In this study, we investigated possible mechanisms which may be responsible for this phenomenon, focusing on p-CdTe:P, hoping that understanding this effect will help us to grow highly conducting p-CdTe:P films [59, 63].

Some possible explanations for this effect in p-CdTe:P are: (i) an artifact of the measurement, especially the capacitance-voltage (C-V) measurement that is used in most cases to observe the carrier concentration gradient, (ii) out-diffusion of the dopant, (iii) in- or outdiffusion of compensating native defects and/or their interaction with the dopant elements and (iv) neutralization of dopants by H₂. Regarding possibility (i), the C-V measurement may show an apparent concentration gradient where none exists either when an insulating compound layer is formed at the surface or when a large density of deep levels are introduced throughout the bulk material during the heat treatment [45, 64]. For possibility (ii), the reaction appears to be too fast to be consistent with literature values of the dopant diffusion constant. If possibility (iii) is to be true, a new model is needed that is applicable to both n- and p-CdTe. The fourth possibility has good experimental evidence [65], but it cannot explain similar results of heat treatment experiments performed in other ambients, without H₂.

To investigate the validity of each possibility suggested above, several experiments including annealing in various ambients and sequential etching are performed. After reviewing the results of these experiments, a possible model is suggested for the compensation of the shallow impurity near the surface in p-CdTe.

2.5.3 Experimental Procedure

Single crystal p-CdTe:P samples [42] (4 x 5 x 1 mm³) were cut from boules and prepared as per Sect. 2.1.1. After chem-mechanical polishing the samples were etched in MeOH-Br (2%) for 4 min and then annealed in various ambients, all at 425°C and for 20 min. Annealing in H₂ was done in a graphite block strip heater, using Pd purified H₂. Annealing under Cd or other ambient vapors was done using ampoules. High purity quartz ampoules were etched in HNO₃-HF(10%) solution and baked under vacuum to drive off moisture before samples were put in. A two zone furnace was used to control the vapor pressures of the Cd and P. After the heat-treatment, In Schottky contacts were applied to the chem-mechanically polished side of the sample and Au semi-ohmic contacts were applied to the back side, both by thermal evaporation in vacuum. Carrier concentrations were obtained from C-V measurements.

In order to check possibility (i), successive etching of a heat-treated sample was done. The In contacts were removed by dipping the samples into conc. HF for about an hour and the sample was then cleaned and etched using a MeOH-Br (0.1%) solution for 30 sec to remove about 0.2 μ m of CdTe. Part of the sample surface was covered by lacquer for protection from etching so the etching depth could be measured by an α -StepTM measurement. Indium contacts were again applied and C-V measurements were made. This process was repeated until the original bulk carrier density value was obtained.

To check possibility (ii), an experiment was designed to separate the two effects that may occur during the heat-treatment; (a) the evaporation of CdTe from the surface which may lead to native defect formation and (b) dopant out-diffusion. A CdTe sample was put in a small quartz ampoule (length = 10 cm, inside diam. = 1.1 cm) with undoped CdTe powder (about 0.7 g). Since the powder has a large surface area, the evaporation of CdTe to reach the equilibrium vapor pressure over CdTe inside the ampoule must be completed in a very short time. Thus, the evaporation of CdTe from the sample could be limited to a very small amount since it can happen only during the short time period before the equilibrium vapor pressure was set up, while the out-diffusion of the dopant remained possible during the whole heat treatment. P would diffuse toward the surface from the bulk, and evaporate at the surface mostly in the form of P₄ at the present temperature.

2.5.3 Results and discussion

The result of the etching experiment is shown in Fig. 22. The carrier density profiles measured in each etching step match with each other very well, and from this result, it is obvious that the C-V data are real, showing a large carrier density decrease near the surface of the heat-treated CdTe. If the carrier density gradient were an artifact due to an insulating surface layer, then the etching experiment would have had to show the sudden disappearance of the gradient as soon as the layer was removed. On the other hand, if deep levels were responsible for the gradient, the same gradient (over the same carrier density range) would appear after etching. The etching results perfectly match

with each other and from this we conclude that the carrier depletion near the surface produced by annealing is a real effect.



Fig. 22. A complete hole density profile of a p-CdTe:P sample annealed in vacuum (10^{-2} Torr) at 425°C for 20 min. The data were obtained by successive etching and C-V measurements.

<u></u>

Figure 23 shows the result of the heat-treatment with CdTe powder present.

These data are compared with both a control sample and a sample annealed in vacuum. While the CdTe annealed in vacuum showed appreciable carrier loss, the sample annealed with CdTe powder showed little change. In this case, free out-diffusion of dopants, if any, was allowed whereas the evaporation of CdTe was minimized. The result suggests that the carrier loss near the surface is related to the CdTe evaporation at the surface of the sample rather than to the out-diffusion of the dopants. In other words, the evaporation of CdTe from the surface creates defects that compensate the acceptors in the region. It is known that Cd evaporates faster than Te because of its higher equilibrium vapor pressure, leaving Cd vacancies behind [65a]. V_{Cd} acts as an acceptor when ionized, so that this species alone cannot compensate any other acceptors. Therefore, it is necessary to know

all the possible defect species in p-CdTe:P to determine which might be responsible for the compensation. The defect species noted in the literature are; (i) $P_{T_{\theta}}$, P_i , T_{e_i} , and V_{Cd} as acceptors, (ii) P_{Cd} , Cd_i , and $V_{T_{\theta}}$ as donors, (iii) P_{Cd} P_i and P_{Cd} V_{Cd} as complex defects.





In order to investigate the variation of the carrier loss as a function of the Cd vapor pressure, CdTe samples were ampoule annealed at various Cd vapor pressures. The result is shown in Fig. 24. It is known [66] that, in the higher Cd pressure regime, Cd interstitials compensate the acceptors. This is evident in Fig. 24. However, in the lower Cd pressure regime, V_{Cd} are expected to form and increase the ionized acceptor concentration if the system were in equilibrium [66]. From Fig. 24, it can be seen that the present system shows the opposite behavior. The present system is not at equilibrium since the annealing temperature is low (425°C) and the time is also relatively short (20 min), so that only kinetically favorable reactions occur. Never-the-less the observations should show the directions of the equilibrium reactions.



Fig. 24. Hole concentrations of p-CdTe:P after annealing at different cadmium vapor pressures at 425°C for 20 min.

Considering that annealing in N₂, Ar, and vacuum were carried out without excess Cd present, it is important to understand the compensation mechanism in the lower Cd pressure regime. One possibility is the formation of P_{Cd} which is a multiple donor. According to the Brouwer diagram made by Selim and Kröger for p-CdTe:P [66], an appreciable amount of P_{Cd} forms in p-CdTe:P annealed in low Cd vapor pressures. This possibility was investigated as follows.

In the higher Cd pressure regime, the phosphorus may take either the interstitial sites (P_i) or the Te sites (P_{Te}) . Both the P_i and P_{Te} are acceptors, so that if we increase the P vapor pressure in this regime, the carrier concentration should increase accordingly. This is illustrated in the following relation between the hole concentration and phosphorus vapor pressure derived from the mass action law and charge neutrality condition;

$$n_h \propto P_{P4}^{1/8} \tag{1}$$

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Since Eq. (1) is derived from the equilibrium conditions whereas the system in this experiment is not at equilibrium, the power of P_{P4} (i.e., 1/8), may not be exactly applicable to the present system. However, we can still use Eq. (1) as a reference for our system and the trend is that as P_{P4} increases, then the hole concentration also increases.

On the other hand, in the lower Cd pressure regime, the phosphorus may take the Cd site (P_{Cd}) by jumping into a Cd vacancy formed by Cd evaporation. P_{Cd} is a multiple donor so that it compensates acceptors in the region. In the same way used for Eq. (1), the concentration of the compensating species (donors) as a function of phosphorus pressure in the low Cd pressure regime is derived assuming that

$$n \approx 3 \left[P_{Cd}^{3+} \right] \tag{2}$$

Then the concentration of the compensating electrons as a function of the phosphorus pressure is given by

$$n \propto P_{P4}^{1/8} \tag{3}$$

The tendency is for more compensation to occur as the phosphorus pressure goes up, according to Eq. (3). To study this possibility, annealing was done at different phosphorus vapor pressures for a given Cd pressure. The formation of a P compound at the surface of the CdTe during this annealing is a formal possibility since both Cd and P are used as the vapor source. From the available thermodynamic data [67-69], we believe that no P compound forms at the surface of the sample as a result of annealing and none was observed visually.

The experimental results are given in Table 1. The results follow the expected tendency, which suggests that P_{Cd} is the compensating species in p-CdTe:P annealed in the lower Cd vapor pressure regime and it also seems to play the same role for the anneal of p-CdTe:P under different ambient conditions (such as in vacuum) because V_{Cd} is believed to form as a result of the annealing in these cases also.

In order to see this point clearly, we annealed Cs doped p-CdTe in vacuum. Cs takes Cd sites to act as an acceptor so that formation of V_{Cd} by annealing does not result in the formation of donor species. The formation of V_{Cd} will increase the hole concentration since it is an

TABLE 1. Hole densities of p-CdTe:P annealed at
various P vapor pressures.

PHOSPHOROUS PRESSURE (P_A) (atm)

	0	3.3 x 10 ⁻⁵	1.0 x 10 ⁻²	1.6 x 10 ⁻¹
Cd PRESSURE (atm)	F	IOLE DEN	SITY (cm ⁻¹	3)
1.0 x 10 ⁻³ 5.0 x 10 ⁻⁷	1.2 x 10 ¹² 1.6 x 10 ¹⁶	 8.1 x 10 ¹⁵	5.6 x 10 ¹⁴	1.9 x 10 ¹⁵ 2.4 x 10 ¹⁵

acceptor species. Fig. 25 shows that the hole concentration of p-CdTe:Cs annealed in vacuum increased as expected, which supports the suggested compensation mechanism. The same crystal annealed in H_2 showed a decrease in carrier concentration, so neutralization of dopant impurities by H_2 is probable since the carrier density decreased for p-CdTe:Cs only when H_2 was used as the ambient.

The possible compensation mechanism for p-CdTe:P during the heattreatment, e. g., in vacuum, is:

 $Cd_{Cd} = Cd(g) + V_{Cd}$ $P_i + V_{Cd} = P_{Cd}$ $P_{Cd} = P_{Cd}^{3+} + 3e.$

This model assumes that most of the P exists in p-CdTe:P as P_i , which is a reasonable assumption because most of the CdTe crystals used are grown with excess Te.

To investigate whether the reverse reaction is possible, we annealed a sample of p-CdTe:P, which had been annealed in vacuum (2×10^{-7} Torr), with CdTe powder. The CdTe powder was used to prevent any further reaction at the surface during the subsequent heat treatment. From the results shown in Fig. 26, it is evident that the reverse reaction is considerably slower.



Fig. 25. C-V data of p-CdTe:Cs samples showing hole density increase by annealing in vacuum. A : annealed in vacuum. B: control. C: annealed in H_2 . All annealing done at 425°C for 20 min.



Fig. 26. C-V data of p-CdTe:P, annealed successively at 425°C under different conditions. A: annealed 20 min. in vacuum, 2×10^{-7} Torr. B: sample A annealed with CdTe powder for 20 minutes, C: sample B annealed with CdTe powder for 5 hr, D: Control.

2.5.4 Summary

The carrier concentration decrease near the surface in p-CdTe:P by heat-treatment was found to be neither an artifact of measurement nor due to out-diffusion of the dopant. We conclude that in-diffusion of V_{Cd}, followed by movement of P to the vacancy sites, forming P_{Cd} (a donor) is the compensating mechanism. This follows from the results of annealing p-CdTe:P in vacuum and p-CdTe:Cs in various ambients. The reaction of the carrier density decrease can be reversed by annealing a previously annealed sample with undoped CdTe powder. Neutralization of Cs dopant impurities by H₂ is probable since the carrier density decreased for p-CdTe:Cs only when H₂ was used as an ambient.

2.6 Solar Cells

Solar cells were prepared by evaporating a two-layer CdS film onto the epitaxial CdTe film to prevent creation of a buried homojunction [70]. The CdS layer adjacent to the CdTe is undoped and acts as a diffusion barrier to prevent the In doping in the top layer of CdS from entering the CdTe. Following the deposition of the p-CdTe films and cooling to room temperature, the samples were removed and immediately placed on a substrate holder and loaded into a vacuum evaporator. A substrate of microscope glass was also loaded onto the substrate holder with the CdTe film, in order to provide a check of the CdS quality and resistivity. The substrates were heated to 200°C, and CdS was evaporated from a Knudsen effusion source at a background pressure of \approx 3 x 10⁻⁷ Torr. An undoped layer of CdS \approx 0.3 µm was deposited, followed by an In doped layer that was $\approx 1 \mu m$ thick. The resistivity of the In doped CdS, as determined from 4-point measurements made on the films grown on the glass, was $\approx 0.04 \ \Omega$ -cm. A schematic of the device is shown in Fig. 27. An In grid was evaporated on the CdS for a front contact. After a 5 minute etch of the back-CdTe surface with dichromate/sulfuric acid/deionized water etch. Au contacts were evaporated onto the back. A Schottky barrier of In was also evaporated onto the CdTe films on an area that was not covered with CdS. Dark and light (AM1.5, 100 mW/cm²) current density-voltage plots were made for the solar cells and V_{oc} and J_{sc} were determined. Quantum efficiency data were measured, current-voltage and capacitance-voltage data were obtained from the Schottky barriers, and carrier density profiles were determined from $1/C^2$ vs. V data taken at 1 MHz.





All the solar cells were prepared using the same two layer n-CdS window configuration. The p-CdTe film configuration varied, being of two basic types: 1) a single layer, with a constant carrier density, and 2) a two layer film, one layer with a constant carrier density, and the other, next to the CdS, without any doping.

Films SC-19 ($T_{sub} = 400^{\circ}$ C) and SC-35 ($T_{sub} = 425^{\circ}$ C) were grown with ion energies of 60 eV and 80 eV respectively, and had carrier densities in the high 10¹⁶ cm⁻³ and low 10¹⁷ cm⁻³ range with flat carrier density profiles. These yielded cells with lower V_{oc} and lower J_{sc} (Table 2). If the ion energy was reduced to 40 eV, as in SC-24, the V_{oc} increased somewhat, but the J_{sc} remained about the same. The low J_{sc} is believed to be due to both relatively small depletion widths and short minority carrier diffusion lengths (L_d), which are due to the presence of a higher density of recombination sites. The low V_{oc} is believed to be due to the large difference between the hole density in the p-CdTe (high 10¹⁶, low 10¹⁷ cm⁻³) and the electron density in the undoped CdS (≈10¹⁵ cm⁻³) [71]. The increase in V_{oc} for SC-24 is believed to be due to the better matching of the carrier densities on either side of the junction.

Cell No.	CdTe Config.	lon Energy (eV)	lon Density (10 ¹⁹ cm ⁻³)	Growth Temp (°C)	Carrier Density (10 ¹⁷ cm ⁻³)	V _{oc} (volts)	J _{SC} (mA/cm ²)	Fill Factor	Efficiency (%)**
19	S *	60	1.62	400	0.7	0.36	5.5	0.51	1.0
23	S	40	0.72	425	0.45	0.55	10.6	0.45	2.6
24	S	40	1.22	400	0.55	0.55	6.6	0.61	2.2
25	S	40	1.78	450	0.35	0.54	10.7	0.55	3.2
35	. S	80	1.55	425	2	0.31	7.0	0.55	1.2
37	т+	80	1.35	450	0.5†	0.60	16.7	0.64	6.2
38	Т	80	1.23	450	0.8	0.50	14.1	0.56	4.0
42	Т	60	0.78	450	0.6	0.63	15.4	0.35	3.4
* 0'	1						41 1	1	

TABLE 2. n-CdS/p-CdTe Solar Cell Parameters

* Single Layer + Two Layer † Carrier density is quoted for the doped layer

** Active area %, ≈AM 1.5, 100 mW/cm²

For films doped at an ion energy of 40 eV and having a flat carrier density profile of $\approx 4.5 \times 10^{16}$ cm⁻³, J_{SC} increased with substrate temperature while V_{oc} remained unchanged (Table 2, SC-23, 24, and 25). Quantum efficiency curves clearly indicate this trend (Fig. 28). The increase in J_{SC} with growth temperature is believed to be due to the annealing out of ion damage, leading to an increase in L_d and a decrease in recombination. Modeling shows that values of L_d ≈ 0.2 -0.4 µm are consistent with the shape of the quantum efficiency curves. Increasing the growth temperature above 450°C however, led to a decrease in the incorporation of the dopant and also to a gradient in the carrier density (see Sect. 2.5).



Fig. 28. Quantum efficiency for three cells for which the CdTe layers were deposited at different T_{sub} .

The best results were obtained with the CdTe films with a two layer configuration (Table 2). In this case a P ion doped CdTe layer was grown on the p-CdTe:P substrate, followed by an undoped CdTe layer. This of course widens the depletion layer. Care must be taken to ensure that the undoped layer is of the proper thickness. Too thick a layer leads to an increase in the series resistance and a decrease in the fill factor. Too thin a layer leads to a decrease in J_{sc} , believed to be due to significant amounts of generation occuring in a region of short diffusion length and high recombination. The optimum thickness for the Fig. 29 shows the light J-V curve undoped layer was about 0.8 µm. for the best cell obtained to date, SC-37. The film was grown at 450°C, with a growth rate of 0.15 μ m/min, an ion current of 0.5 μ A/cm² and an ion energy of 80 eV. The doped portion of the CdTe film had a carrier density of 4×10^{16} cm⁻³, while the undoped portion of the film had a carrier density of 5 x 10^{14} cm⁻³. The V_{oc} was 0.60 volts, and the J_{sc} was 16.7 mA/cm². The fill factor was 0.64 and the overall cell efficiency under simulated sunlight (\approx AM 1.5, 100 mW/cm²) was 6.2% (active area basis). Fig. 30 shows the quantum efficiency of cell SC-37 and it is considerably higher than those for the cells of Fig. 28.



Fig. 29. Dark and light J-V curves for cell SC-37.



Fig. 30. Quantum efficiency of cell SC-37.

Other cells grown with the two-layer CdTe configuration also showed larger V_{oc} and J_{sc} (Table 2, SC-38, 42). The advantage of the undoped CdTe layer is threefold: 1) the undoped CdTe is a better match to the undoped CdS, leading to a larger V_{oc} [1], 2) the undoped CdTe apparently has a longer diffusion length and less recombination than the doped CdTe, leading to a larger J_{sc} , and 3) the depletion layer in the CdTe is wider, also increasing the collection efficiency and hence, J_{sc} . Films can be grown at lower temperatures because generation occurs in a region with no ion damage. recombination

In future work with solar cells we intend to increase the relative carrier density level in both the CdS and CdTe at the interface, to see what effect the relative carrier density has on the optimization of V_{oc} . Other cell configurations are being considered. One possibility is inverting the cell, which includes initially depositing the two CdS layers, doing a heat treatment to clean the surface, and then depositing the two layers of CdTe [72].

2.7 Doping experiments on Polycrystalline material

2.7.1 Bicrystals

Before extensive study of polycrystalline films grown by IAD, consideration was first given to bicrystal films, for which individual grain boundaries could be studied. Bicrystal substrates were cut from an n-type CdTe boule that was grown by II-VI Compounds, Inc. [73]. Two pairs of bicrystal substrates were prepared, with each pair having the same orientations. The n-type substrates were chosen so that 4point, along-the-film resistivity measurements could be made on the epitaxial films. Laue pictures were taken of each grain in the boule in order to orient the samples, and also to give an idea of the mismatch between the grains (Fig. 31). The substrates were ground and polished as described in Sect. 2.1.1. IAD doped films were grown on the bicrystals, with an attempt to optimize the doping for each bicrystal. There was some difficulty in accomplishing this due to differing film thicknesses on each side of the grain boundary (because of the dependence of the film growth rate on crystallographic orientation).



Fig. 31. Orientation of grains of bicrystals.

Four-point measurements were made across the grain boundary and also within each grain (Fig. 32a). The four-point measurements across the grain boundaries were done as a function of temperature, both in the dark and under illumination from a microscope lamp (\approx 40 mW/cm²), going from room temperature to 140°C. After the temperature measurements, In Schottky barriers were evaporated onto each side of the film. A gold ring contact was etched around the Schottky barrier using a solution of gold chloride, enabling J-V and C-V measurements to be made (Fig. 32b). Three-point measurements were made with the configuration, to avoid problems with contact resistance in the gold ring. Carrier density values were determined from the C-V measurements, and in conjunction with the resistivity measurements, hole mobilities were calculated. Grain boundary activation energies were determined from the plots of the across-the-grain-barrier conductivity versus temperature.

Orientation data for the two best films are shown in Table 3. Sample GB-3 had large misorientation between the grains, while GB-6 had comparatively little mismatch. The mobilities inside the grains were about what was expected for bulk CdTe. Fig. 33 contains plots of conductivity vs. inverse temperature, both in the dark and in the light, for the two films, and Table 4 contains the grain boundary conductivity activation energies for the films, both in the dark and in the light. The activation energies for both samples for the dark and the light fell



Fig. 32. Contact configurations for bicrystal measurements. a) For resistivity measurement. b) Modification for capacitance measurement.

TABLE 3. Orientation and Transport Data							
Sample	Θ1	Θ2	Carrier Density (cm ⁻³)	Mobility (cm ² /V-sec)	N _{ion} (cm ⁻³)		
GB-3	43°	44°	4 x 10 ¹⁶ 7.5 x 10 ¹⁶	51 47	0.79 x 10 ¹⁹ 0.65 x 10 ¹⁹		
GB-6	- 7°	17°	3.5 x 10 ¹⁶ 3 x 10 ¹⁶	10 26	1.08 x 10 ¹⁹ 0.95 x 10 ¹⁹		



Fig. 33. Conductivity vs. inverse temperature for bicrystals.

TABLE	4. G	irain E	Boundary Activa	tion Energ	gies and	Resistances
Sample	Θ1	Θ2	Carrier Density (cm ⁻³⁾	Activation Dark (eV)	Energy Light (eV)	Resistance (Ω-cm ²)
GB-3	43°	44°	4 x 10 ¹⁶	0.66	0.24	3.4 x 10 ³
GB-6	7°	17°	3.5 x 10 ¹⁶ 3 x 10 ¹⁶	0.2	0.13	8.3

within the range of what was seen in an earlier study [74]. Sample GB-3, with the larger misorientation, shows the larger activation energy. The grain boundary specific resistance (Table 4) increases strongly as the misorientation increases.

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2.7.2 Polycrystalline thin films

To study the effects of IAD on polycrystalline films several different groups of films were grown (Table 5). Initially all films were grown on high purity graphite (grade DFP-3-2, Poco Graphite, Decatur, TX). All substrates were scored with a SiC knife and cleaved to 10 x 12 mm². Substrates were blown with dry nitrogen to remove dust, and then loaded in the substrate holder in a manner similar to the single crystal substrates. For the first group of seven films, the ion current was the variable, and the substrate temperature was kept at 400°C, the ion energy was 60 eV, and the ion current was varied between 0 and 1.5 μ A/cm². A second group of films had the ion energy as the variable, with the substrate temperature again kept at 400°C, the ion current maintained at about $1.2 \,\mu$ A/cm², while the ion energy varied between 40 and 100 eV. The third group of samples was prepared with the substrate temperature varying between 200°C and 500°C, while the ion energy and ion current were kept at 60 eV and at about 1.2 μ A/cm², respectively. The films were on the order of about 12-14 µm thick, with the exception of the sample grown at 450°C, which was 5 µm thick, and the sample that was attempted at 500°C, for which no film grew. Grain size was typically $\approx 2.0 \ \mu m$.

 Table 5.	Principal Polycrystal	line Film Dep	position Series	
Series	Substrate Temp. (°C)	lon Density (cm ⁻³)	lon Energy (eV)	
 1	400	0 — 2.8 x 10 ¹⁹	60	
2	400	2.2 x 10 ¹⁹	40 — 100	
3	200-500	2 x 10 ¹⁹ *	60	

* Except for the samples for 450°C for which the ion density was 5.4 x 10^{19} cm⁻³.

Schottky barriers of In were evaporated onto the films, with the graphite substrate as the back contact. Finally, J-V and C-V measurements were made on all the films.

Overall, the films were highly resistive, being on the order of 5 x 10^7 Ω -cm. With the exception of a film grown at 0.067 μ A/cm², all the

films from the first group grown with ion current as the variable had nearly linear J-V curves. For the film grown with 0.067 μ A/cm², the difference in the current density between reverse 1 volt and forward 1 volt was only about half an order of magnitude (Fig. 34). Varying the ion energy had little effect on the J-V curves, and C-V measurements indicated a carrier density of between 3 and 4 x 10¹⁴ cm⁻³ for all the films. The biggest change was seen in varying the substrate temperature. The film grown at 200°C had a linear J-V curve, and as the temperature increased the J-V curves became more and more rectifying. Fig. 34 shows the difference between the films grown at 400°C and at 450°C. The carrier density, as determined by C-V measurements, went from 2.5 x 10¹⁴ cm⁻³ at 400°C to 9 x 10¹⁴ cm⁻³ at 450°C.



Fig. 34. Log J vs. V for samples grown at 400°C and 450°C with J_{ion} =0.08 $\mu\text{A/cm}^2$ and V_{ion} = 60 V.

Further experiments were done to explore the films grown at 450°C using a different type of graphite substrate [Poco vitreous coated grade DFP 2-3], since it was smoother and resulted in the growth of

smoother films. For either type of substrate 450°C was the maximum temperature at which it was possible to still grow a film. A series of films was prepared at $T_{sub} = 450$ °C, with the ion current varying between 0 and 1.2 μ A/cm² for an ion energy of 60 eV. One film was grown at an ion current of 5.5 μ A/cm² and an ion energy of 100 eV, the higher ion energy being needed to obtain the higher ion current. It showed a completely linear J-V characteristic and a resistivity of \approx 2.4 x 10¹⁰ Ω -cm. The forward-bias portion of the J-V curves for the other samples from this group are seen in Fig. 35. As the ion current increases, the forward bias portion of the J-V curve becomes lower and lower, indicating an increase in resistivity. Fig. 36 shows a plot of resistivity, as determined from the high forward-bias rolloff of the J-V curves, as a function of ion current.

Resistivity as a function of temperature was measured for two of the PX films using a Au dot with a surrounding Au ring. The current path was from the dot to the graphite substrate plus from the graphite to the Au ring, i.e., two transits through the thickness of the film. The results shown in Fig. 37 show little difference between samples 'Graph27', with no doping, and 'Graph28' with $J_{ion} \approx 1.1 \,\mu A/cm^2$. The data for the undoped sample indicate an activation energy of 0.45 eV, whereas the doped sample gives 0.74 eV. These values can be compared with 0.66 eV obtained for the bicrystal with large mis-orientation. Since the resistivity is dominated by the grain boundaries with the largest values of barrier height, this is a reasonable correlation. The small change with light, compared to the bicrystals, is due to the fact that very little light gets to the region under the contacts through which current is flowing.



Fig. 35. J-V curves for samples grown at $T_{sub} = 450$ °C and $V_{ion} = 60$ V (except for the highest ion current, for which $V_{ion} = 100$ V). Running variable is J_{ion} .



Fig. 36. Resistivity of the diodes of Fig. 35, as a function of N_{ion} .



Fig. 37. Conductivity as a function of inverse temperature.

Carrier density (p), measured by C-V techniques, is plotted against J_{ion} in Fig. 38 for samples grown at 400 and 450°C. p shows an approximately linear increase with J_{ion} . The linear nature of the J-V curves does call into question the C-V measurements for some of the films. However, for those films where there is some rectification, increasing the ion current does seem to indicate an increase in the carrier density. Even for these films, however, the carrier density varied between the mid to high 10^{14} cm⁻³.

The effective mobility μ , calculated using the p values of Fig. 38 and the resistivity values of Fig. 36, and plotted in Fig. 39, shows a strong decrease with increasing J_{ion} which is approximately of the form μ = A exp(- B J_{ion}), where A and B are constants. Since the effective mobility is controlled by the grain boundary barrier potentials in these PX materials, we conclude that increasing J_{ion} increases the barrier height. The mechanism for this is not known, but we can surmise that compound formation at the grain boundaries may be the cause.



Fig. 38. Carrier density vs ion current for PX films on graphite deposited at 400 and 450° C and $V_{ion} = 60$ V. (The 450°C samples are those of Fig. 35 and 36.)





3. DISCUSSION

3.1 Doping CdTe by IAD

The evidence for doping of epitaxial CdTe films with As and P ions is conclusive. In the work done so far we observed a smooth increase of p for increasing ion flux to a maximum of $5-8 \times 10^{16}$ cm⁻³ for As and $\approx 2 \times 10^{17}$ cm⁻³ for P ions. It is concluded from the P ion current density, the growth rate of the films, and the measured carrier density, about 1% of the impinging ions are incorporated into the film as electrically active dopants. Judging from preliminary SIMS results most of the missing P is re-evaporated or sputtered away. Thus, for the SIMS sample $\approx 97\%$ of the incoming dopant is rejected at the surface, 1.5% is electrically active, and the remaining 1.5% is electrically inactive. This picture is consistent with the observation that the ratio of the films if all the impinging ions were incorporated) becomes larger for higher growth rates, presumably because the dopant atoms are incorporated before they have a chance to re-evaporate.

The increase of p with increasing V_{ion} (up to a point) and the decrease of p with increasing T_{sub} suggest that the incorporation of dopant is a balance between an input of shallow ion implantation and ion burial, and an output by re-evaporation of the dopant from the growth surface. In addition, the electrical activity of the dopant that is finally incorporated depends on the in-diffusion of Cd vacancies and the subsequent movement of dopant atoms to those sites where they act as donors, compensating the existing doping (e.g., P_{Cd}). Thus the electrical activity of the dopant is expected to decrease with increasing T_{sub} .

The carrier density falls off abruptly for J_{ion} values larger than that producing the maximum p (Fig. 11, 14, 15). The threshold for this falloff is near $J_{ion} \approx 0.5$ -1.5 μ A/cm², and some of the highest p values and also some of the lowest values—are found at this J_{ion} . For films deposited with higher J_{ion} than that producing the maximum p, hysteresis is seen in the J-V and C-V curves and the p vs W_d profile has an apparent gradient, suggesting the presence of a large density of deep states. The p falloff is equally evident in P and As doped films. While no definitive explanation is possible at this point, we advance the possibilities of (a) extensive self compensation due to incorporation of P or As on Cd sites where they behave as donors, (b) the production of compensating defects by ion damage, or (c) compound formation. With regard to the first possibility, the effect would of course depend on the stoichiometry of the growing surface, and film growths with excess Cd pressure would help to elucidate this. The second possibility is more difficult to justify since the ion damage should be proportional to the ion flux and this should not lead to such a rapid falloff. The third possibility, compound formation, may increase the self compensation, e.g., the formation of Cd_3P_2 would also deplete the Cd density, promoting more self compensation. Additional SIMS measurements and XTEM analysis may help to explore this last possibility.

The evidence for a large density of deep traps is also seen in the films deposited with V_{ion} values ≥ 100 V. Given the results in Sect. 2.4, the effect here is one of ion damage, probably with the creation of a number of different kinds of states, some of which are donor-like and, in large densities, lead to type conversion.

3.2 Application to solar cells

From the solar cell results described in Sect. 2.6, it is evident that placing moderate to highly ion doped CdTe layers adjacent to the junction produces devices with only moderate quantum efficiencies ($\eta_Q \approx 35-55\%$). The quantum efficiency depends on both the minoritycarrier diffusion length L_d and the depletion layer width W_d, with the depletion layer acting as a layer with an extremely long effective L_d. The η_Q does increase with increasing T_{sub}, suggesting that either the depletion layer widths have increased and/or that increasing the temperature anneals out more recombination centers. In comparison, similar cells made on single-crystal material, with comparable depletion layer widths, show larger η_Q , up to $\approx 80\%$. (About 18% of the light is reflected, since these cells have no anti-reflection coatings.)

When an intervening layer of undoped CdTe is deposited on top of the IAD layer, then η_Q increases, becoming comparable with single crystal values. The undoped CdTe is depleted and this large increase in W_d should result in a major increase in η_Q . We can postulate that the undoped material has a longer L_d, but it is unclear how much this would contribute to the increase in η_Q .

The open-circuit voltage is also increased by the deposition of an intervening, undoped layer, but again the cause is unclear.

From the above discussion it appears that IAD homoepitaxial films with moderate to high doping have lower minority carrier diffusion lengths (Ld) than those of single-crystal material. Since the mobilities of these films are comparable to those of single-crystal material, the implication is that the minority carrier lifetimes in the films are lower, but increase with increasing T_{sub} . The use of undoped films does provide high quantum efficiency but it is unclear whether this is due to an increase in depletion layer width or to an increase in L_d , or both. In order to utilize IAD as an experimental tool to measure junction properties as a function of carrier density, methods will have to be developed to obtain long minority carrier lifetimes in the material. These methods might include (a) using lower ion energies, (b) using as high a substrate temperature as possible, (c) annealing the material before or after the formation of a junction, (d) the possible beneficial effects of controlling the stoichiometry during IAD deposition by the use of additional Cd or Te sources, and (e) using some sort of passivation method during IAD deposition.

3.3 Polycrystalline films

While work on polycrystalline films on amorphous substrate must be considered as preliminary, the indications are that the doping densities achieved so far by IAD are insufficient to overcome the effects of the grain boundary barriers.

Measurements on IAD doped bicrystals show that the grain boundary potential barrier heights are in the range of 0.2 to 0.7 eV and increase with increasing misorientation of the grains, in agreement with measurements of others [74]. If we take the measured grain boundary conductances measured for the bicrystals from Sect. 2.7.2, and assume a grain size of 2.5 μ m, bulk resistivities of 3 x 10⁴ to 10⁷ Ω -cm are predicted, which is reasonably consistent with observed values for our PX material on graphite.

While the carrier densities obtained in the bicrystal experiments were in the mid 10^{16} cm⁻³ range, polycrystalline (PX) thin films grown on graphite substrates under similar conditions yielded carrier densities in the $10^{14} - 10^{15}$ cm⁻³ range and bulk resistivities in the mid $10^7 \Omega$ cm range. The open-circuit voltage is also increased by the deposition of an intervening, undoped layer, but again the cause is unclear.

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The J-V characteristics of In diodes on the PX material are poor, becoming almost linear at high Jion, but somewhat more rectifying as Jion is decreased, although the dependence is not strong. The ion energy appears to have little effect on the diode characteristics over the range 40-100 eV. Substrate temperature has the largest effect and rectification increases substantially for higher T_{sub}. The through-thefilm resistivity, as measured from the J-V characteristics of In diodes on the PX material, *increases* for increasing J_{ion}. Since the average carrier density also increases with Jion, the effective mobility in the film, determined by grain boundary potential barriers, decreases The conductivity activation energy increases from 0.45 eV stronaly. for an undoped film to 0.74 eV for a highly doped film. Although the activation energy is not a direct measure of the potential barrier height, these data suggest that the potential barrier height increases with J_{ion}, perhaps due to compound formation at the grain boundaries. Increasing substrate temperature causes a decrease in the throughthe-film resistivity.

The apparent increase in barrier height with J_{ion} mentioned above suggests that a method for passivation of the grain boundaries, such as deposition in a partial pressure of H₂, might provide lower resistivities.

4. CONCLUSIONS

The following conclusions can be drawn from this research:

- 1. Doping levels in p-CdTe homoepitaxial films up to $\approx 6 \times 10^{16} \text{ cm}^{-3}$ for ion-assisted deposition with As ions and to $\approx 2 \times 10^{17} \text{ cm}^{-3}$ for P have been achieved using ion energies of 30-80 eV.
- 2. For a growth rate of $\approx 18 \ \mu$ m/hr, a substrate temperature of 400°C, and an As ion energy of 30 eV, a maximum in doping density appears near an ion current of $\approx 1 \ \mu$ A/cm², corresponding to a doping efficiency (the ratio of the density of electrically active dopant atoms to the density of impinging ions) of about 0.5% in the deposited film. Typically, for P ions the ratio is somewhat higher: 0.7% at 7 μ m/hr and 0.4% at 1 μ m/hr with ratios of 1.5% sometimes observed.

- 3. Preliminary SIMS results suggest that, for hole densities around 10¹⁷ cm⁻³, most of the dopant is not incorporated into the film, but that most of the dopant incorporated is electrically active.
- 4. Ion currents above 1.5 μ A/cm² and/or ion energies above 50 to 100 eV produce damaged films with large densities of deep states, as evidenced by large reverse bias currents for In/p-CdTe diodes and hysteresis in the C-V data.
- 5. In separate experiments, Ar ion impingement with $J_{ion} \approx 28 \ \mu A/cm^2$ on single crystal p-CdTe caused type conversion of the surface, with a threshold ion energy of 80-100 eV.
- 6. Experiments with solar cells showed poor quantum efficiencies when highly IAD doped films were the major site of photogeneration of carriers, implying short minority-carrier diffusion lengths (L_D) for this material. (This does not imply that the short L_D must always result from ion-assisted doping of p-CdTe, however. For example, it might follow from doping with the particular Cd+Te vapor stoichiometry that prevailed during deposition.)
- 7. IAD deposition of PX films on graphite substrates results in an apparent increase in p with increasing J_{ion}, however, the resistivity of the films increased. Evidently the carrier transport in these films is dominated by the grain boundary barriers and the level of doping that has been achieved thus far is insufficient to overcome the effects of the barriers.
- 8. The decrease in near-surface carrier density observed on heating p-CdTe:(P or As) in various ambients (vacuum, H_2 , Ar, etc.) is shown to be a self-compensation mechanism due to out-diffusion of Cd vacancies followed by movement of the dopant atoms into the vacancy where they act as donors.
- 9. The ease with which CdTe self-compensates suggests that control of the micro-stoichiometry of the vapor species above the growing film during deposition is important in controlling the doping.

5. DIRECTIONS FOR FURTHER RESEARCH

The research described here was certainly not exhaustive and several rich areas for further research are apparent:

- 1. Characterization of ion damage. The nature of the ion damage, if present, is unclear at this time. Deep level analysis as a function of ion energy as well as XTEM of homoepitaxial layers would shed more light on this, as would post-deposition anneals of thick films.
- Investigation of the cause of the apparent decrease in minority carrier diffusion length with increasing ion-assisted doping. Identification of the energy level of the recombination centers might elucidate their cause and adjustment of stoichiometry during IAD deposition (e.g., by adding a Cd source) could possibly eliminate them.
- 3. Defining the role of stoichiometry. The analysis of Kröger et al. suggests that the doping mechanism should be quite sensitive to the micro-stoichiometry at the growing surface. The use of a separate, auxiliary Cd or Te source to change the Cd/Te ratio in the vapor should elucidate this. Also the use of Cs or Na as a dopant should help to explain the role of Cd vacancies in the ion-assisted doping mechanism.
- 4. Polycrystalline (PX) thin films. The cause of the apparent increase in grain boundary barrier height with increasing ion current is unknown at this time, but compound formation at the boundaries is a possibility. Experiments such as those mentioned below should help to elucidate this and provide methods for either holding the barrier heights constant or decreasing them: (a) examining the effect of changing the stoichiometry of the vapor species above the growing film, thus altering the formation of possible compounds, (b) using other dopants, especially from column I, which may not form such compounds, and (c) using hydrogen passivation during IAD deposition. Carrier densities in the high 10¹⁷ to low 10¹⁸ cm⁻³ range will probably be necessary to overcome the grain boundary potential barriers and provide low resistivity polycrystalline material.
- 5. Continued improvement of reproducibility. Reproducibility of the hole density was a formidable problem, especially in the early stages of the research. The incorporation coefficient of the dopant

ions does not appear to depend on crystallographic orientation, however, it was found that crystallographic orientation had to be controlled because the differing growth rates for different directions gave rise to different effective ion densities. Better temperature control also substantially improved the reproducibility. In the later stages of research stepped doping profiles were valuable in obtaining data for identical deposition conditions.

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APPENDIX I: SUMMARY OF FURTHER RESEARCH DURING 9/23/89 TO 5/10/90

Paul Sharps (supported by an AT&T fellowship) continued to work on ion-assisted doping after the close of this contract period (6/30/89) and finished his Ph.D. thesis research about 6/9/90. During this time he further refined the measurements of hole density as a function of ion current and voltage, and substrate temperature, made correlations with SIMS and TEM results, and made additional device studies on IAD films on single-crystal substrates. Paul's thesis, which is now available, describes this work in detail and an IEEE Photovoltaic Specialist's paper [A-1] and his journal article [A-2], planned for publication in the fall of 1990 (probably in the Journal of Applied Physics), will summarize the research. A brief summary is also presented here.

Data for carrier density vs. ion dose were extended from those of Fig. 11 and Fig. 15A and compared with SIMS measurements of P density, done by Sally Asher at SERI. A series of samples that were ion doped with P to various levels were examined by SIMS and the resulting data were referenced to that of a "standard" vertical-Bridgman-grown single-crystal sample which had been doped with P. The hole density in the standard was determined from $1/C^2$ vs V data and the electrical activity of the dopant was assumed to be 1.0 giving a P density of 2.5 x 10¹⁶ cm⁻³. The resulting curves are shown in Fig. A1. Given the parallelism between the P density by SIMS and the measured carrier density in the upward sloped portions, the offset between the curves is probably due to an over-estimation of the electrical activity of P in the reference "standard". The data suggest that the electrical activity of the incorporated P is approximately unity for the upward-sloped portion of the carrier density curve. For the plateau portion of the curve, more P is incorporated but the electrical activity drops, presumably because of a compensation mechanism, such as P going onto Cd sites where it acts as a donor (Sect. 2.5).

This situation is similar to that for the carrier density vs. introduced P for single crystals grown from the melt. In the growth-from-the-melt case a plateau is reached at $\approx 2 \times 10^{17}$ cm⁻³ and no further increase in carrier density is seen for larger amounts of P. In this case the electrical activity of P for introduced P less than 2×10^{17} cm⁻³ is also approximately unity [7, 66]. Higher hole densities can be introduced into single crystals, but apparently only metastably...When these

crystals are annealed, the carrier density drops to $\approx 2 \times 10^{17}$ cm⁻³. For example, Gu et al. [A-3] obtained p-CdTe:P with a hole density $\approx 6 \times 10^{17}$ cm⁻³ by quenching the as-grown ingot. {A notable exception is Li doping, for which hole densities sufficiently high to make tunneling contacts (probably $\approx 5 \times 10^{18}$ cm⁻³) can be obtained by diffusion.





A further consequence of the data of Fig. A1 is a reinforcement of the conclusion that most of the P (\approx 98%) is not incorporated into the growing film but is rejected and probably re-evaporates.

At an ion dose of $\approx 5 \times 10^{19}$ cm⁻³, the carrier density drops precipitously, and, since the SIMS determined P density is still proportional to the ion dose (the incorporation ratio hasn't changed), another compensating mechanism must be coming into play. This was suspected to be the formation of precipitates (which, if inherently ntype, would compensate the P acceptor doping), so XTEM studies were done on selected samples. However, the XTEM results, obtained by John Goral at SERI, show no evidence of precipitates. This second compensating mechanism might be due to the rate of ion damage exceeding the rate of annealing out of this damage at this ion current (Sect. 2.4).

John Goral's XTEM results did show a large density of dislocations in the films, which appear to originate near the p-CdTe-substrate/p-CdTe-film interface. These dislocations may serve to explain the low minority carrier lifetimes observed. Although the XTEM results show that the film is lattice matched with the substrate and that the substrate has no apparent dislocations, at this point no satisfactory explanation for the presence of the dislocations is available.

The dependence of carrier density (p) on ion energy was re-measured and a data set with less scatter obtained (Fig. A2) (cf. Fig. 12). These data show an almost constant p over the range of ion energies from 60 to 300 eV. These data do not contradict the data of Section 2.4 (which shows ion damage down to $E_{ion} \approx 100 \text{ eV}$), however, since the Section



Fig. A2. Carrier density vs. ion energy. Ion dose = 5×10^{18} cm⁻³, T_{sub} = 400°C, growth rate = 10 µm/hr, and film thickness ≈ 10 µm.

2.4 data were obtained with room temperature substrates, while the data of Fig. A2 are for $T_{sub} = 400^{\circ}$ C, at which the ion damage could be annealed out. In addition, the data of Sect. 2.4 were obtained with much higher ion currents.

The dependence of hole density on substrate temperature T_{sub} was also refined, as shown in Fig. A3 (cf. Fig. 13). For growth temperatures < 350°C, the carrier density drops dramatically, perhaps because T_{sub} is too low to anneal out ion damage. If ion damage is the compensating mechanism then this is what would be expected. There was little change in carrier density for 350° < T_{sub} < 450°C. The decrease when T_{sub} exceeded 500°C may again be attributed to increased re-evaporation of P from the surface resulting in decreased incorporation.





In normal Schottky barriers, the thermionic component usually dominates at moderately high forward-bias, this being finally limited at higher bias by the series resistance of the device (R_s) (see Sect. 2.3.2). For our In/p-CdTe (epi)/p-CdTe (bulk) devices, R_s should be the sum of the bulk resistance of the film, the interface resistance, the

bulk resistance of the substrate, and the back contact resistance. (The spreading resistance of the In contact is neglected.) The resistance of the portion of the film within the depletion layer is negligible because of its thinness. In such diodes the resistivity of the undepleted portion of the film can be estimated by determining Rs at high bias, when the dynamic resistance of the diode is negligible, provided the contact, interface, and bulk substrate resistance can be measured separately. In examining a series of diodes (Fig. A4) we found that the bendover of the log J vs. V curves at high bias appeared as an R_s that varied systematically with the carrier density, but indicated much higher Rs than could be accounted for by summation of the resistances of the components of the device. Moreover, on more careful examination it was found that (a) the bendover followed a J α Vⁿ dependence with n \approx 3 to 5, indicative of space-charge limited current, (b) the resistance of the bulk substrate and film (by calculation ≈ 1.3 to 1.5 Ω -cm², assuming a mobility of 50 cm^2/V -sec) and of the interface between them (by measurement) were negligible on the scale of Fig. A4, and (c) it was difficult to justify such a large voltage drop anywhere in the postulated junction structure. Indeed, pulsed forward biases up to ≈ 10 V were applied to one diode without breakdown, and the same general J α Vⁿ dependence was seen.



Fig. A4. Log J vs. bias voltage (dark) for In/p-CdTe diodes. Ion energy = 60 eV, T_{Sub} = 400°C, growth rate = 10 µm/hr, and growth time ≈ 1 h. Measured carrier density is shown as a running parameter. Sample FR-54-3 Dt is a diode on a single-crystal substrate without an IAD doped film.

This apparent anomaly is now being investigated, since it appears in other junctions from our work as well as that of other researchers. This and the some of the other anomalies* generated by the work are tantalizing and we feel that their explanation will add valuable insights to the understanding of CdTe.

- * 1. The mechanism for the strong decrease of hole density at high Jion.
 - 2. The reduction of minority carrier lifetime in the ion doped films.
 - 3. The origin of the dislocations near the film-substrate interface.
 - 4. The origin of the increase of resistivity in polycrystalline films with increasing J_{ion}.

APPENDIX II: A BRIEF HISTORY OF THE PROGRAM

Since the beginning of research on CdTe-based devices, workers have been frustrated by the difficulty in doping the material, especially ptype. This added substantially to the difficulty in making low resistance contacts to the material. Also it would be highly advantageous to dope thin films (both epitaxial and polycrystalline) and to be able to readily make comparisons between CdTe devices with a variety of carrier densities. In late 1984, one of the authors (ALF) discussed the problem with Prof. John Thornton, who suggested that ionization of the dopants might make it possible to incorporate them and that an ion source could readily be made, following the example of Rockett and Greene [40]. A proposal was written and funded and we set to work. In our literature research we were pleased to note that ion doping had been successful with MBE grown Si and GaAs.

We began by using As, since the vapor pressure seemed ideal, and with rather large ion currents, $\approx 100 \ \mu\text{A/cm}^2$. Although we determined that plenty of As was getting into the CdTe films, doping was not apparent, suggesting that the range of ion currents that produce doping might be small. This was indeed the case and only after lowering the ion current several times, down to $\approx 1 \ \mu\text{A/cm}^2$, were we able to obtain controllable doping. To our knowledge this was the first time ionassisted doping had been used with any of the II-VI semiconductors.

By this time other researchers obtained high p-type doping in CdTe by MOCVD and photon-assisted doping (as described in Sect. 1.2.2). Also it was becoming increasingly obvious that efficient polycrystalline CdTe solar cells could be made using insulating CdTe in p/i/n junctions. However, we felt that ion-assisted doping research was still a valuable endeavor to increase our knowledge of CdTe, especially in studying the effects of dopant incorporation from the vapor and effects of carrier density on junctions and contacts.

From single-crystal experience we had expected that phosphorous would yield higher doping densities and we knew that it is considerably less toxic than As. With some apprehension we put red phosphorus in the ion source and were surprised to find that it was quite controllable and yielded doping densities up to 2×10^{17} cm⁻³. After considerable effort Paul Sharps was able to master the early scatter in the data and obtain the clear-cut relationships shown in Appendix I.

Perhaps the most important product of our endeavor has been graduate training.

- Kuo-Fu Chien, Engineer's Degree, Thesis title: "The Effects of Low Energy Ion Bombardment on Single Crystal CdTe," June 1987.
- David Oberman, supported 12.5% time Sept. 1988 through June 1989. David investigated the "TRIM" code for computer simulation of ion interaction with single crystals and used it to simulate the impingement of P ions on CdTe.
- Paul Sharps (supported by an AT&T fellowship), Ph. D. Thesis title: "Ion-Assisted Doping of p-CdTe Films," May 1990.
- Michael Grimbergen, (replaced K-F. Chien), supported from Sept. 1987 through Dec. 1989 when he moved to our a-Si:H program. While on the program he accomplished the following:
 - (a) He built a second, back-up ion source.
 - (b) He investigated the feasibility of combining hot-wall vacuum evaporation (HWVE) with ion-assisted doping. He found that they were mutually exclusive for the normal vapor pressure range of HWVE because the mean-free-path of the ions in the vapor would be too short. However a coaxial ion source could be used at the lower end of the pressure range to ionize all the constituent vapors (e.g., Cd, Te₂, and P) in a combined system.
 - (c) Mike investigated the vacuum deposition of n-ZnSe:CI on GaAs by co-evaporation using ZnSe, ZnCl₂, and Zn sources. He obtained epitaxial films and measured along-the-film resistivities as a function of stoichiometry (excess Zn), obtaining values as low as $1 \ \Omega$ -cm.
 - (d) He made a preliminary design for a liquid N_2 shrouded, ionassisted deposition fixture with two Knudsen cells and one ion gun.
- Donghwan Kim, supported since April 1987. Ph.D expected ca. 6/91. (Tentative thesis title: "Growth and doping of CdTe films: effects of photons, ions, and stoichiometry variations").

Another product of the research was a very successful one-day symposium on photon and ion-assisted doping that was attended by 40 experts from all over the United States. An agenda is included as Fig. A5.

DEPARTMENT OF MATERIAL SCIENCE AND ENGINEERING

SYMPOSIUM

ION AND PHOTON ASSISTED GROWTH AND DOPING OF SEMICONDUCTOR MATERIALS

THURSDAY, AUGUST 18, 1988 LOCATION: GEOLOGY 320 AUDITIORIUM

The Department of Materials Science and Engineering has organized a one-day symposium on ion and photon assisted growth and doping of semiconductor materials, sponsored by the Solar Energy Research Institute. The symposium will focus on those effects and phenomena in which the ions and/or photons interact directly with the growing surface of the material being deposited. In the case of ions this means increased sticking and incorporation for dopants, including the possibility of shallow ion implantion, and the growth of metastable phases because of the increased energy at the growing surface. In the case of photons this includes the interaction of electrons and holes from the photo- excited growing film with the growth and/or doping processes, as well as photolytic reactions at the surface.

OPENING

- 9:00 Welcome and opening remarks Materials Synthesis for the '90's
- 9:20 Advanced Materials Synthesis at SERI
- 10:05 BREAK

OVERVIEW AND THEORY

10:25 Overview of Ion-Assisted Growth and Doping, Theory and Research

ION-ASSISTED GROWTH

- 11:25 Ion-assisted growth of superconductor layers
- 12:00 LUNCH*
 - PHOTON-ASSISTED GROWTH AND DOPING
- 1:30 Photon-assisted doping of CdTe and MnCdTe
- 2:30 BREAK
- 2:50 Photon, ion, and field assisted oxidation of Si

ION-ASSISTED DOPING

3:50 Ion-assisted doping of CdTe

<u>CLOSING</u>

- 4:20 Open Discussion
- 4:50 Wrap up and review

Stig Hagstrom, Chairman Dept. of Materials Science & Engr., SU

Ted Ciszek Solar Energy Research Institute

Joseph Greene Dept. of Metallurgy, Coordinated Science Lab, & Materials Research Lab., University of Illinois

Nancy Missert Applied Physics, SU

Jan Schetzina Dept. of Physics, No. Carolina State Univ. North Carolina State University

William Tiller Dept. of Materials Science & Engr., SU

Alan Fahrenbruch Dept. of Materials Science & Engr., SU

R.H. Bube Dept. of Materials Science & Engr., SU

Fig. A-5. Agenda for PIAD Symposium.

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APPENDIX III: PAPERS, ARTICLES, AND PRESENTATIONS

<u>Papers</u>

- A.L. Fahrenbruch "Ohmic contacts and doping of p-CdTe," Solar Cells **21**, 399 (1987).
- <u>A.L. Fahrenbruch</u>, A. Lopez-Otero, K-F. Chein, P. Sharps, and R.H. Bube,"Vapor phase and ion-assisted doping of thin film p-CdTe," Proc.19th IEEE Photovoltaic Spec. Conf. (1987), p. 1309.
- K-F. Chien, A.L. Fahrenbruch, and R.H. Bube, "Characterization of ion damage on p-CdTe surfaces," J. Appl. Phys. 64, 2792 (1988).
- <u>P. Sharps</u>, A. L. Fahrenbruch, A. Lopez-Otero, and R. H. Bube, "Solar cells made from p-CdTe films grown with ion-assisted doping," Proc. 20th IEEE Photovoltaic Spec. Conf. (1988), p. 1641.
- D. Kim, A. L. Fahrenbruch, and R. H. Bube, "Effects of heat treatment on the surface carrier density in p-CdTe," Proc. 20th IEEE Photovoltaic Spec. Conf. (1988), p. 1487.
- <u>P. Sharps</u>, A. L. Fahrenbruch, A. Lopez-Otero, and R. H. Bube, "Thin films of p-CdTe grown with ion-assisted doping," Proc. Materials Research Society, Boston, MA, Dec. 1988.
- A.L. Fahrenbruch, K-F. Chien, D. Kim, A. Lopez-Otero, P. Sharps, and R.H. Bube, "Ion-assisted doping of p-CdTe," Solar Cells **27**, 137 (1989).
- <u>P. Sharps</u>, A. L. Fahrenbruch, A. Lopez-Otero, and R. H. Bube, "Thin film p-CdTe grown by ion-assisted doping," Proc. 21th IEEE Photovoltaic Spec. Conf. (May, 1990), Orlando, FL, to be published.
- P. Sharps, A.L. Fahrenbruch, A. Lopez-Otero, and R.H. Bube, "Ion-assisted doping of p-CdTe films," submitted for publication, J. Appl. Phys.

<u>Talks</u>

<u>P. Sharps</u>, A. L. Fahrenbruch, A. Lopez-Otero, and R. H. Bube, "Thin films of p-CdTe grown with ion-assisted doping," Materials Research Society, Boston, MA, Dec. 1988.

SERI Reports and Meetings

SERI Branch Annual Reports, 1986, 87, 88, 89.

SERI Polycrystalline Film Solar Cell Reviews: 1987 and 89 ('89 published in Solar Cells, above).

SERI Advanced Research and Development Meeting, 1989.

Symposium on Ion- and Photon-Assisted Growth and Doping of Semiconductor Materials Presented at Stanford University on August 18, 1988. A one day symposium with talks by Stig Hagstrom, Ted Ciszek, Joseph Greene, Nancy Missert, Jan Schetzina, William Tiller, Alan Fahrenbruch, and Richard Bube.

APPENDIX REFERENCES

- A-1. P. Sharps, A. L. Fahrenbruch, A. Lopez-Otero, and R. H. Bube, "Thin film p-CdTe grown by ion-assisted doping," Proc. 21th IEEE Photovoltaic Spec. Conf. (May, 1990), Orlando, FL, to be published.
- A-2. P. Sharps, A.L. Fahrenbruch, A. Lopez-Otero, and R.H. Bube, "Ionassisted doping of p-CdTe films," submitted for publication, J. Appl. Phys.
- A-3. J. Gu, T. Kitahara, K. Kawasami, and T. Sakaguchi, J. Appl. Phys. 46, 1184 (1975).

Document Control Page	1. SERI Report No. SERT/TP-211-3907	2. NTIS Accession No. DE90000358	3. Recipient's Accession No.
4. Title and Subtitle			5. Publication Date July 1990
Vapor Deposition, Final Subcontract Report			6.
7. Author(s) R.H. Bube, Principal Investigator			8. Performing Organization Rept. No.
9. Performing Organization Name and Address			10. Project/Task/Work Unit No.
Department of Materials Science and Engineering Stanford University Stanford, California 94305-2205			11. Contract (C) or Grant (G) No. (C) _{XB-5-05009-4} (G)
12. Sponsoring Organization Name and Address Solar Energy Research Institute			13. Type of Report & Period Covered Technical Report
Golden, Colorado 80401-3393			^{14.} 9/1/85 - 8/30/89
15. Supplementary Notes SERI Technical Monitor: C. Leboeuf, (303) 231-1066			
doping during chemical vapor deposition of CdTe and (2) determine the influence of co-depositing ionized dopant atoms on the growth and structural and photoelectronic properties of the deposited films. In p-CdTe homo-epitaxial films, we controlled doping up to about 6×10^{16} cm ⁻³ and 2×10^{17} cm ⁻³ for ion-assisted depositions with As and P ions, respectively. At a growth rate of approximately 0.1 μ m/min, a substrate temperature of 400°C, and an ion energy of 60 eV, a maximum doping density was found near an ion current of 0.6 μ A/cm ² . Related studies included elucidating the role of low-energy ion damage in the ion-assisted doping process, and investigating the decrease in carrier density near the surface of p-CdTe upon heating in vacuum, H ₂ , or Ar. We demonstrate the ability to make carrier density profiles and to grade junctions, and we present preliminary results from polycrystalline p-CdTe films grown on graphite and alumina substrates. We also present solar cells prepared using the p-CdTe as the collector area and n-CdS as the window layer, and we examine their photovoltaic parameters for different carrier densities and configurations in p-CdTe.			
17. Document Analysis a. Descriptors Photovoltaics ; solar cells ; doping ; vapor deposition			
b. Identifiers/Open-Ended Terms			
c. UC Categories 273			
18. Availability Statement			19. No. of Pages
National Technical Information Service U.S. Department of Commerce 5285 Dept Benel Beed			88
Springfield, Virginia 22161		20. Price A05	

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Form No. 0069 (6-30-87)

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