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Crystalline Silicon Materials Research

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ABSTRACT

Our recent silicon photovoltaic (PV) materials research activities are summarized. We developed a novel iodine-vapor transport technique that produces polycrystalline Si layers of 10-40 µm thicknesses on glass substrates, and at a high growth rate of ~3 µm/min. The layers exhibit large grain sizes of 5-20 µm and 5 µs minority carrier lifetime. Results from our on-going study of metal impurity and impurity-dopant pair defect effects on lifetime indicate strong recombination at Fe-Ga pair defects. Transient photoconductance simulations by finite element analysis were carried out for our surface probe lifetime measurement approach. Several cooperative research activities with Si-PV companies are discussed.

1. Introduction

Our recent research activities have focused on three topics: thin-layer silicon growth on foreign substrates; understanding the effects of transition metal impurities on minority charge-carrier lifetime and Si material performance in PV devices; and assisting the c-Si PV industry with selected materials research problems. The sections below elaborate on these research areas.

2. Thin-Layer Silicon Growth

Nucleation on non-Si substrates requires a growth process with sufficient driving force to overcome a substantial nucleation barrier. We originated a chemical-vapor transport method that achieves this using an iodine disproportionation reaction [1]. It offers the possibility of atmospheric operation in an open system and is capable of depositing large-grain polycrystalline Si layers on foreign substrates at a fast rate and an intermediate temperature.

Our system consists of a vertical reactor with iodine and source silicon placed at the bottom. The source silicon temperature is maintained at 1000°-1200°C. The top of the reactor is kept slightly above the melting point of iodine and is capped with a removable purge inlet and outlet assembly that blankets the region above a gravitationally confined iodine column with either inert gas or hydrogen. A movable sample holder suspends the substrate near the top of the reactor during purging and precursor formation. The substrate is then lowered to a position where the temperature is about 900°C for thin layer Si growth. We have used several high-temperature glass ceramics as substrates, as well as heavily doped silicon.

During the entire purge and run cycle, the heavier iodine and silicon iodide gas species stay in the lower section of the reactor tube and are trapped at the top by a cooler cloud of condensates. A hydrogen purge gas forms a gas curtain between the reacting gases and the atmosphere, allowing open system operation without significant loss of iodine or reduced iodine partial pressure as is the case in a normal open system involving a carrier gas.

Our experiments show that the disproportionation reaction between SiI_2 and SiI_4 is responsible for silicon transport from high to low temperature in the atmospheric pressure reactor. Fig.1 illustrates the reaction mechanism.

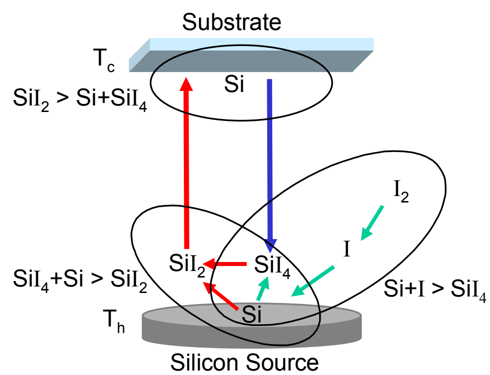

Fig. 1. Iodine vapor transport reaction mechanism

Grains as large as 20 µm are easily obtained, as shown in Fig. 2. Higher temperature favors larger grains. The typical growth rate is 3 µm/min and strongly depends on the substrate and source temperatures. A minimum substrate temperature of about 800°C is needed to start the deposition. Growth rates as high as 10 µm/min are observed for a source/substrate temperature of 1200°/1000°C. An effective minority-carrier lifetime of about 5 µs was measured, implying a diffusion length far exceeding the 10-40 µm layer thickness.

Fig. 2. SEM photo of the surface of the Si layer

3. Impurity Effects and Lifetime

There are dramatically different effects on minority-carrier lifetime (τ) and PV device performance for different transition metal impurities. For example, Cu is relatively benign, Ti has a very strong degrading effect, and Fe has an intermediate effect. In addition, transition metal impurities participate with the typically-used boron dopant to form pair defects. There is increased interest in alternative p-type dopants because boron has been linked to short-term, slight efficiency degradation. There are also increased efforts to "upgrade" metallurgical-grade Si (MG-Si) for solar-grade feedstock use. Thus, there is a need to better understand differences in Shockley-Read-Hall recombination of the different metallic impurities and to characterize defect-pair behavior with other p-type dopants such as Ga.

We have initiated a systematic study of Fe, Ti, and Cu behavior in otherwise high-purity silicon, with and without Ga doping. Dislocation-free, float-zoned Si was deliberately doped with Fe and Ga during growth. Crystal properties were documented by deep-level transient spectroscopy and annealing studies [2]. The typical τ of Fe-Ga co-doped crystals (0.4 μs) was dramatically lower than that of crystals doped with similar amounts of either Fe alone (12 μs) or Ga alone (1,400 μs), contrary to the τ behavior at low injection of Fe-B pair defects (see Table I). Thermal dissociation of Fe-Ga pairs increased τ, confirming a stronger carrier-recombination activity at Fe-Ga pairs than at interstitial Fe. Defect energies (relative to the valance band) equal to 0.10 and 0.21 eV were observed for Fe-Ga co-doped samples. The corresponding hole-capture cross-sections were found to be 3×10^{-16} cm^2 and 6×10^{-15} cm^2.

Table I. Minority-Carrier Lifetime of Dislocation-Free <100> FZ Single Crystals Doped with Fe and Ga

Crystal	Resistivity (Ω-cm)	Ga (cm^{-3})	Fe (cm^{-3})	Lifetime (μs)
41121 a	3.5	3.8×10^{15}	0	>1400
51129-1	24,000	0	1.2×10^{14}	12
70515	6	2.2×10^{15}	4.8×10^{11}	2.2
51212-la	4.1	3.3×10^{15}	1.3×10^{14}	0.40
51212-lb	1.4	1×10^{16}	1.3×10^{14}	0.34

Localized photon excitation and photoconductance detection on a silicon ingot surface are a convenient and cost-effective means to measure minority-carrier lifetimes, and we reported on an industrially-rugged surface-probe system for the measurement at the last review meeting [3]. Using the classical drift-diffusion-recombination model, we successfully performed three-dimensional transient photo-conductance simulations by finite element analysis to examine the correlation between measured effective lifetime and true bulk lifetime. For two-probe detection and localized photon excitation, we found that the majority carriers determine the ambipolar diffusion and drift with a small spatial separation between the minority and the majority carriers. Various combinations of surface-recombination velocity and bulk lifetime were calculated using specified values for absorption coefficient, minority carrier diffusivity, and excitation-spot size to enable the derivation of an empirical formula for practical lifetime measurements.

4. Research on Industry Si Materials Problems

We completed activities under a cooperative research and development agreement (CRADA) with EBARA Solar, Inc. (ESI) on the dendritic-web ribbon-growth process. An ESI web-growth furnace was set up and operated at NREL. The research resulted in major improvements in the success rate of the web-growth start-up procedure, an intricate process involving coplanar propagation of two dendrites from a single seed dendrite. An improved crucible design for better shallow-melt stability and thermal isolation of the melt replenishment process from the ribbon-growth region was also achieved. The other aspect of the work involved x-ray topographic analysis of ribbon defects and stresses. In the course of the work, the production rate of silicon dendritic web at ESI more than doubled. Overcoming start-up problems and gaining greater insight into the web-growth initiation process has lead to increased throughputs.

Another collaborative project is underway with GT Equipment Technologies, Inc. in the area of silicon feedstock deposition. This work is examining modified chemical-vapor deposition (CVD) techniques with the potential of greatly enhanced deposition rates. In addition, we are engaged at NREL in several approaches for purifying MG-Si to useful levels for solar-grade feedstock.

5. Summary

Our project emphasizes silicon materials research that will complement work in industry by examining next-generation silicon growth technologies (such as iodine vapor transport), by understanding the effects of grown-in defects and impurities (such as transition metals and metal-dopant pair defects) on silicon minority-carrier lifetime and material performance, and by assisting the c-Si PV industry with selected silicon materials problems (such as the pending feedstock availability problem or specific crystal-growth issues). Some of our recent progress in these areas has been presented. Additional details about our research can be found on our website at http://www.nrel.gov/silicon/.

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