

Optical, structural and transport properties of reactively sputtered ZnTe:N

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ABSTRACT

Nitrogen-doped ZnTe produced by reactive sputtering is attractive as a possible component layer of a back contact for CdTe-based solar cells. It has the advantages of being free of copper, having a close valence band match to CdTe, and can be doped heavily p-type with substitutional nitrogen. In addition, because it is transparent to photons below 2.2 eV, it is a candidate for a back contact/tunnel junction in tandem cells using CdTe or CdZnTe top cells. In this study we have characterized films of ZnTe:N sputtered with various N₂/Ar ratios. These films have been studied by x-ray diffraction (XRD), atomic force microscopy (AFM), Raman spectroscopy, optical absorption, variable angle spectroscopic ellipsometry (VASE) and the Hall effect. We also report optical emission spectra of N₂ during reactive sputtering.

1. Introduction

This paper describes some results of our research funded through the High Performance PV Program of NREL. The award to The University of Toledo includes close participation with First Solar as a major lower-tier subcontractor. The effort focuses initially on the exploratory development of II-VI cells suitable as top cells in double junction tandem devices with, e.g., CIS as a bottom cell. Major elements of this effort include studies of CdZnTe and development of transparent back contacts and tunnel junctions for the top cell. We expect to fabricate both two-terminal and four terminal prototype devices.

In the present study, we present the characteristics of reactively sputtered films of ZnTe doped with N. We are investigating this copper-free p-type material as a possible component of a tunnel junction or transparent back contact. We have achieved ~9% cells with good stability using ZnTe:N layers on vapor transport deposited CdTe [1,2]; however, better performance will require ZnTe with increased conductivity. We describe here optical emission spectroscopy (OES) during the reactive sputtering process as well as electrical measurements and Raman scattering on the films. In addition, we have done x-ray diffraction, atomic force microscopy, optical absorption, and spectroscopic ellipsometry measurements (at IEC).

2. Optical emission from the sputter plasma

We have earlier obtained films with carrier concentrations of up to $5 \times 10^{18} \text{ cm}^{-3}$ with sputter conditions of: 40 W

rf power, 400 C substrate temperature, 18 mTorr pressure, and 63 sccm flow. We are presently re-optimizing the growth process while monitoring the plasma optical emission for appropriate excited state species of N and N₂. Fig. 1 shows a typical emission spectrum obtained from the target surface of the first positive band of N₂ ($B^3\Pi_g \rightarrow A^3\Sigma_u$). The strongest vibrational transition in Fig. 1 is for $v'=9 \rightarrow v''=5$ at 590.6 nm. This vibrational state lies only 2.8 eV below the 10 eV dissociation energy of N₂. Since the $^3\Sigma_u$ state is metastable, significant density should impact the growth surface. Due to its low dissociation energy we expect better incorporation of atomic N from the metastable N₂ than from ground state N₂. In a similar situation, Jordan, et al, [3] have provided evidence that this molecular state is advantageous for MBE growth of GaN using a plasma nitrogen source. They argue that the metastable molecule can much more easily release the binding energy of N in GaN than can atomic N, because the second atom can carry away excess energy from the growth interface. We are presently spatially tracking this emission to the film surface and correlating this emission with film characteristics as sputter parameters are varied.

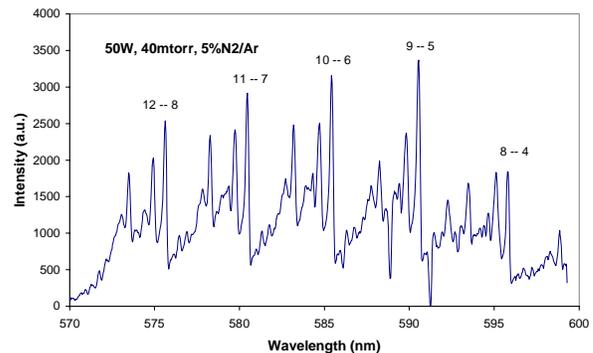


Fig. 1. Example of OES spectrum from first positive band of N₂ during reactive sputtering. Ar lines were subtracted.

3. ZnTe microstructure vs N/Ar ratio during sputtering

Electrical measurements [2] have indicated that the conductivity increases only slightly with increasing N/(Ar+N) gas mixture from 2 to 5% as decreases in mobility almost balance increases in carrier concentration. This partly prompted the AFM, XRD, and Raman measurements described here.

The evolution of the microstructure with increasing N₂ gas fraction is illustrated by the two AFM images of Fig. 2

for 0% and 3% N₂. Analyses show mean grain diameters of 134 nm and 38 nm, respectively.

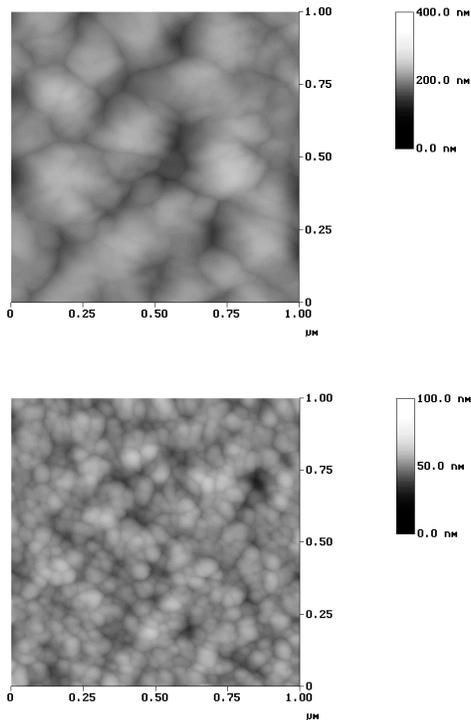


Fig. 2. AFM images of 0.5 μm thick films of ZnTe (upper) and ZnTe:N (lower) grown with 3% N₂ in the sputter gas.

The crystallographic texture was studied by x-ray diffraction. Details of the XRD measurements will be presented elsewhere. The crystallographic orientation parameter, the strain, and the average grain size are shown in Table 1. Δa_0 is inferred from the Nelson-Riley-Sinclair-Taylor method for lattice parameter determination and particle size is inferred from the diffraction peak widths by the Scherrer method. The film orientation was determined by the Harris method normalizing the hkl peak intensities to those of a randomly orientated powder. $p_{111} > (<) 0$ indicates preferred (suppressed) orientation along $\langle 111 \rangle$.

Table 1. XRD analyses (UT0...5 indicates N₂ fraction)

Sample	Orientation Parameter p_{111} (N)	$\Delta a_0 \pm 0.0009$ (Å)	XRD Particle Size (nm)
UT0a	7.0 (9)	+0.0146	125
UT1a	5.4 (9)	+0.0217	35
UT2a	0.4 (4)	+0.0211	14
UT3a	0.4 (5)	+0.0204	10
UT5a	0.3 (5)	+0.0181	8

Note that increasing N₂ in the sputter gas decreases grain size as seen both by AFM and XRD, but also strongly decreases the normally strong $\langle 111 \rangle$ crystallographic texture of these films.

Raman scattering shows a strong 205 cm⁻¹ LO peak and its overtone and a small feature at the 170 cm⁻¹ position of the TO mode. Consistent with heavy doping, the TO mode appears to be increasingly screened and shifted toward the TO mode with 1% and 3% N₂ in the sputter gas. However, the broad peaks also could indicate a transition to an amorphous or nanocrystalline phase. It is possible that the N₂ is inhibiting the film nucleation on the glass substrates and we are presently trying to improve the grain size and mobility of these films as well as obtain further increases in doping density.

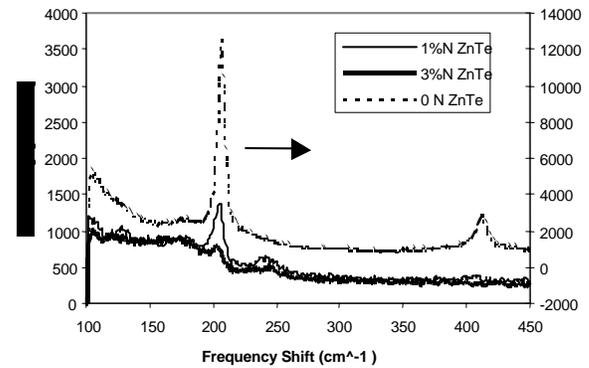


Fig. 3 Room temperature Raman spectra obtained with 514 nm excitation.

All films exhibit optical transmission ~75% and an absorption edge located at ~2.2 eV. The spectroscopic ellipsometry showed some broadening of this E₀ fundamental edge with increasing N, but the E₁ and E₂ direct transitions near 4 eV were particularly strongly broadened and shifted to lower energy—again indicating poor crystallinity and/or surface deterioration. We find that low temperature annealing in air generally increases the film conductivity while producing no observable change in morphological, structural, or optical properties—possibly indicating a decrease in grain boundary barrier heights.

Further work is in progress to clarify the N-dependence of the film microstructure, and further optimize the conductivity of these p-type ZnTe layers.

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