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Nitrogen doping of ZnTe and its influence on CdTe/ZnTe interfaces

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The properties of nitrogen doped ZnTe films and *in situ* formed heterointerfaces to CdTe were investigated using photoelectron spectroscopy and electrical measurements. The *p* doping of ZnTe with nitrogen is controlled during physical vapor deposition with an additional nitrogen plasma source. The resistivity was determined by four-point measurements and a minimum resistivity of $\rho=0.04\ \Omega$ cm was found. The valence band offset of the CdTe/ZnTe interface is $E_{\text{VBO}}=0.05$ eV. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2459589]

CdTe thin film solar cells promise a high potential of good conversion efficiencies of more than 16% (Refs. 1 and 2) with a low cost production process. A good Ohmic contact to the absorber layer without electrical losses is needed for efficient solar cells. Previous studies have shown significant limitations for CdTe/metal contacts. In high efficiency CdTe solar cells ohmic contacts are typically prepared by diffusion of copper to form a thin space charge layer, which can easily be tunneled. Copper is a fast migrating impurity in CdTe and this may lead to a degradation of cell properties.[3,4] In addition, back contacts are formed by applying an etching step with a Br_2/methanol solution or mixed nitric and phosphoric acid.[2,5] The elimination of the wet chemical etching step prior to the back contact deposition would be an important effort to simplify in-line solar cell production. Also, back contacts, which reflect electrons from passing the interface, would be favorable especially for *n-i-p* devices.[6] Highly nitrogen doped ZnTe may provide a promising opportunity for forming a low resistance copper-free back contact without an etching step.[7,8] Carrier concentration up to $p>10^{20}$ cm^{-3} are reported for plasma nitrogen doped ZnTe.[9–11]

Experiments were carried out in the Darmstadt Integrated System for Solar Research, which combines several deposition chambers with multitechnique surface analysis systems.[12] This allows for sample preparation and surface analysis without breaking the vacuum to avoid contamination or modification by air. Nitrogen doped *p*-ZnTe films deposited by thermal evaporation of the compound were prepared using a Tectra plasma ion source inserted into the deposition chamber. Layers of $0.1-1\ \mu$m thickness are grown at $T=320-400\ ^{\circ}$C substrate temperature, at a growth rate ranging between $3-25$ nm/min. The plasma source operated in the atom source mode produces atomic nitrogen from an electron cyclotron resonance plasma. The production of atoms is enhanced by increasing the pressure in the plasma chamber to $p_{N_2}=10^{-5}-10^{-4}$ mbar. All layers are grown either on borosilicate glass or on indium tin oxide coated glass substrates. Photoelectron spectroscopy studies have been performed using a VG Escalab 250 surface analysis system with a monochromatized Al anode x-ray source [x-ray photoelectron spectroscopy (XPS), $h\nu=1486.6$ eV] and a He discharge lamp [ultraviolet photoelectron spectroscopy (UPS), $h\nu=21.22$ eV]. ZnTe:N layers grown with dif-

ferent deposition parameters such as substrate temperature or deposition rate were investigated.

The contact properties of the CdTe/ZnTe:N interface with evaporated ZnTe:N have been examined by stepwise deposition of ZnTe:N onto CdTe substrate and XPS measurements after every deposition step. Highly doped ZnTe: N was deposited with a source temperature of $T=680\ ^{\circ}$C at $T=350\ ^{\circ}$C substrate temperature. This corresponds to a rate of 4 nm/min at these settings. The plasma source was operated at a vacuum pressure of $p_{N_2}=1\times10^{-5}$ mbar and $I=50$ mA magnetron current.

The resistivity of the prepared ZnTe:N films were determined with four-point measurements with a linear contact arrangement taking into account the geometrical correction factor. The thickness of the films was measured with a Siemens Dektak profilometer.

ZnTe films deposited at varying substrate temperatures show different Te/Zn ratios investigated with XPS. An excess of tellurium in the XPS core levels was detected at a lower substrate temperature, but no additional phase was found by x-ray diffraction (XRD) in the deposited ZnTe films. The ratio of the Te$3d_{5/2}$ and Zn$2p_{3/2}$ emissions of ZnTe layers deposited at different substrate temperatures is shown in Fig. 1. A decreasing Te/Zn ratio can be noticed with increasing substrate temperature up to a temperature of $T=300\ ^{\circ}$C. At higher temperature the ratio varies only slightly around a ratio of ≈1.25. Presumably amorphous Te
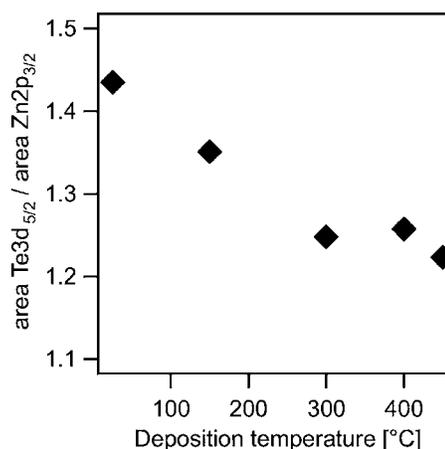

FIG. 1. Intensity ratio of the Te$3d_{5/2}$ and Zn$2p_{3/2}$ emissions of ZnTe layers deposited at different substrate temperatures.

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TABLE I. Deposition parameters and measured resistivity for nitrogen doped ZnTe films.

No.	p 10^{-5} mbar	T_{sub} °C	ρ (Ω cm)	Deposition rate nm/min
1	$\cdots$	25	5	8.2
2	0.5	315	0.25	6.7
3	1	315	0.06	7.2
4	0.5	375	0.07	5.6
5	5	375	0.04	4.1
6	5	375	1.8	25
7	1	425	0.15	6.2
8	10	425	0.4	4

is enriched at the grain boundaries of the ZnTe polycrystalline films at lower temperature.

In Table I the deposition parameters and measured resistivities for the evaporated ZnTe:N layers are shown. The lowest resistivity of $\rho=0.04$ Ω cm was found with a deposition rate of 4.1 nm/min at $T=375$ °C substrate temperature. Baron *et al.* reached a doping level of ZnTe:N layers of $(N_A-N_D)\approx 10^{20}$ cm^{-3} with a resistivity of $\rho=5\times10^{-3}$ Ω cm (Refs. 9–11) and Amin *et al.* reached a resistivity of $\rho=0.045$ Ω cm.[13] The resistivity of the ZnTe with nitrogen is found to be less influenced by the N_2 pressure than by the growth rate of the ZnTe. The flux of nitrogen atoms onto the growth surface is given by the aperture and flux of the plasma source and is obviously affected little by the total pressure. The flux of atoms and possibly excited molecules limit the growth rate of the ZnTe films to achieve a high doping concentration. The resistivity of the ZnTe:N films increases again at substrate temperatures higher than $T=375$ °C.

In all surface and interface studies reported before, the Fermi level at the CdTe surface is found at $E_{VBM}\approx0.6-1$ eV (Refs. 8 and 14–19) above the valence band maximum, which is rather unfavorable for the solar cell. Here we have investigated interface formation by the depo-
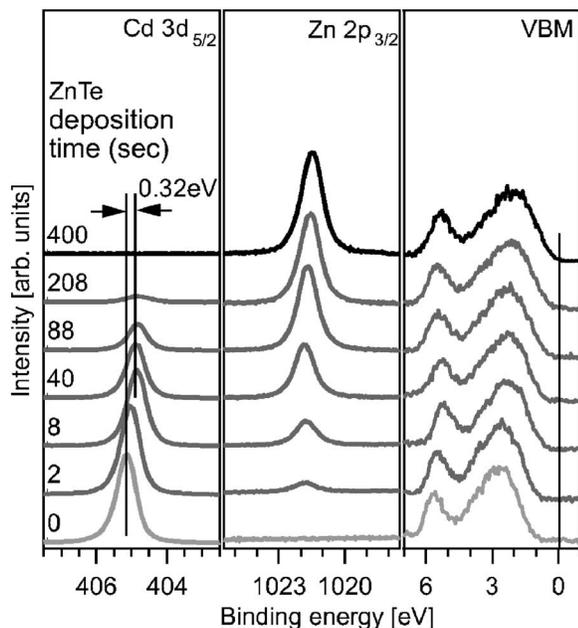

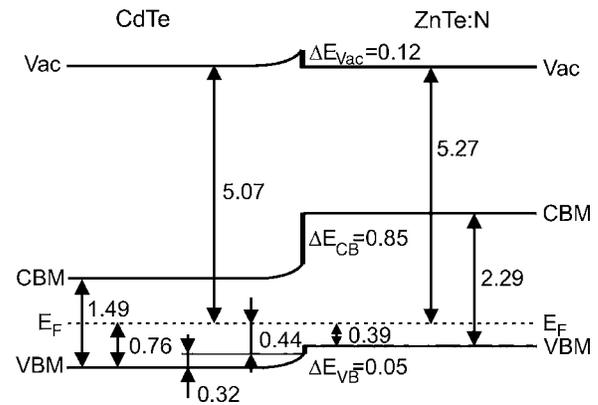FIG. 2. Cd$3d_{5/2}$ and Zn$2p_{3/2}$ core levels from a CdTe surface with increasing ZnTe:N coverage.

FIG. 3. Band energy diagram of the CdTe/ZnTe:N interface as determined by photoelectron spectroscopy. All values are given in eV.

sition of highly *p*-doped ZnTe:N films. The CdTe substrates were prepared by a closed space sublimation (CSS) process at a substrate temperature of $T\approx(530\pm15)$ °C and a source temperature of $T=635$ °C. XPS core-level lines for different ZnTe:N deposition times onto the CdTe substrate are shown in Fig. 2. With increasing ZnTe coverage a decreasing Cd$3d_{5/2}$ emission and increasing Zn$2p_{3/2}$ emission can be seen. After a deposition time of $t=400$ s, no Cd emission remains in the spectra. No chemical reaction can be observed. The binding energies of the core levels with respect to the binding energies of the valence band maximum for CdTe and ZnTe are BE$_{VBM}$(Cd$3d_{5/2}$)=404.39±0.07 eV and BE$_{VBM}$(Zn$2p_{3/2}$)=1021.11±0.07 eV, in good agreement to previous measurements.[8]

A valence band offset of $E_{VBO}=0.05$ eV±0.1 eV is determined for the CdTe/ZnTe:N interface which is in agreement to previous investigations of the interface made by physical vapor deposition or sputtering[7,8] (Using bulk band gaps of 1.49 eV for CdTe and 2.29 eV for ZnTe, the valence band offset corresponds to a conduction band offset of $E_{CBO}=0.85\pm0.1$ eV.) Before ZnTe:N deposition the Fermi level at the CdTe surface is found at $E_{VBM}=0.76$ eV above the valence band maximum. In contrast to previous investigations the Cd$3d_{5/2}$ core-level emission is strongly shifted about $\Delta E=0.32$ eV to lower binding energies with ZnTe:N deposition. This is the result of a band bending in the CdTe substrate towards the Fermi energy resulting in a valence band position in the CdTe substrate of $E_F-E_{VBM}\approx0.44\pm0.1$ eV. No band bending in the ZnTe:N film is detected. The Fermi level of highly doped *p*-ZnTe is found at $E_F-E_{VBM}=0.39$ eV in the valence band spectra (Fig. 2); a work function of $\phi=5.27$ eV was determined using the secondary electron cutoff of the UPS spectrum. The resulting band energy diagram is shown in Fig. 3.

Nitrogen doped *p*-ZnTe as a direct contact layer provides promising properties for the formation of a low resistance back contact to CdTe. Evidently the chemical saturation of most interface dangling bonds at the CdTe/ZnTe interface possibly leads to a passivation of the CdTe surface. This passivation inhibits mostly a Fermi level pinning of the CdTe surface. However, the large lattice mismatch between ZnTe and CdTe about $\approx6\%$ (Ref. 20) must still be compensated by an appropriate mechanism. Additional experiments also at single crystalline surfaces are needed to further clarify this point.

[1] J. Britt and C. Ferekides, Appl. Phys. Lett. **62**, 2851 (1993).

[2] C. S. Ferekides, D. Marinskiy, V. Viswanathan, B. Tetali, V. Palekis, P. Selvaraj, and D. L. Morel, Thin Solid Films **361**, 520 (2000).

[3] K. D. Dobson, I. Visoly-Fisher, G. Hodes, and D. Cahen, Sol. Energy Mater. Sol. Cells **62**, 295 (2000).

[4] D. L. Bätzner, A. Romeo, M. Terheggen, M. Dobeli, H. Zogg, and A. N. Tiwari, Thin Solid Films **451–452**, 536 (2004).

[5] D. L. Bätzner, R. Wendt, A. Romeo, H. Zogg, and A. N. Tiwari, Thin Solid Films **361**, 463 (2000).

[6] W. Jaegermann, A. Klein, J. Fritsche, D. Kraft, and B. Späth, Mater. Res. Soc. Symp. Proc. **865**, F6.1 (2005).

[7] D. Rioux, D. W. Niles, and H. Höchst, J. Appl. Phys. **73**, 8381 (1993).

[8] B. Späth, J. Fritsche, F. Säuberlich, A. Klein, and W. Jaegermann, Thin Solid Films **480**, 204 (2005).

[9] T. Baron, S. Tatarenko, K. Saminadayar, N. Magnea, and J. Fontenille, Appl. Phys. Lett. **65**, 1284 (1994).

[10] T. Baron, K. Saminadayar, S. Tatarenko, H. J. Lugauer, A. Waag, and G. Landwehr, J. Cryst. Growth **185**, 415 (1998).

[11] T. Baron, K. Saminadayar, and N. Magnea, J. Appl. Phys. **83**, 1354 (1998).

[12] J. Fritsche, A. Klein, and W. Jaegermann, Adv. Eng. Mater. **7**, 914 (2005).

[13] N. Amin, A. Yamada, and M. Konagai, Jpn. J. Appl. Phys., Part 1 **41**, 2834 (2002).

[14] D. Kraft, B. Späth, A. Thissen, A. Klein, and W. Jaegermann, Mater. Res. Soc. Symp. Proc. **763**, B3.3 (2003).

[15] D. Kraft, B. Späth, A. Thissen, A. Klein, and W. Jaegermann, Third World Conference on Photovoltaic Energy Conversion, 2003, Vol. 1, p. 450–453.

[16] D. Kraft, U. Weiler, A. Thissen, Y. Tomm, A. Klein, and W. Jaegermann, Thin Solid Films **431/432**, 382 (2003).

[17] D. Kraft, M. Campo, M. Beerbom, T. Mayer, A. Thissen, A. Klein, and W. Jaegermann, Mater. Res. Soc. Symp. Proc. **668**, H7.5 (2001).

[18] J. Fritsche, T. Schulmeyer, D. Kraft, A. Thissen, A. Klein, and W. Jaegermann, Appl. Phys. Lett. **81**, 2297 (2002).

[19] J. Fritsche, D. Kraft, A. Thissen, T. Mayer, A. Klein, and W. Jaegermann, Thin Solid Films **403–404**, 252 (2002).

[20] Y. H. Kim, I. J. Kim, S. D. Lee, K. N. Oh, S. K. Hong, S. U. Kim, and M. J. Park, J. Cryst. Growth **214**, 225 (2000).