

X-ray absorption near edge structure investigation of vanadium-doped ZnO thin films

M. Faiz ^{a,*}, N. Tabet ^a, A. Mekki ^a, B.S. Mun ^b, Z. Hussain ^b

^a Surface Science Laboratory, Physics Department, KFUPM, Dhahran, Saudi Arabia

^b Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

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Abstract

X-ray absorption near edge structure spectroscopy has been used to investigate the electronic and atomic structure of vanadium-doped ZnO thin films obtained by reactive plasma. The results show no sign of metallic clustering of V atoms, +4 oxidation state of V, 4-fold coordination of Zn in the films, and a secondary phase (possibly VO₂) formation at 15% V doping. O K edge spectra show V 3d–O 2p and Zn 4d–O 2p hybridization, and suggest that V⁴⁺ acts as electron donor that fills the σ^* band.

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1. Introduction

Zinc oxide is being the object of intense investigation owing to its attractive applications in optoelectronics. Transition metal-doped ZnO has the potential to be a multifunctional material with coexisting magnetic, semiconducting, electromechanical, and optical properties [1]. Ferromagnetism in diluted magnetic semiconductors is one of the interesting problems of this century in condensed matter physics. Vanadium-doped ZnO (Zn_{1-x}V_xO) shows ferromagnetism above room temperature upon electron doping [2–4]. Such a high Curie temperature is appealing for its applications in spintronics devices. Understanding the electronic structure is a prerequisite for understanding the high-temperature ferromagnetism in these materials.

X-ray absorption near edge structure (XANES) spectroscopy is a powerful local probe for the electronic structure as well as the atomic structure of materials. It probes the empty energy bands by measuring transitions from core levels, and does not require a crystalline sample. Element specificity and symmetry selection rules are some of the powerful aspects of the technique. In this work we have used XANES to investigate the electronic structure of vanadium-doped ZnO thin films.

2. Experimental details

Vanadium-doped ZnO films of less than 1- μ m thickness were deposited on unbiased glass substrate at room temperature by reactive plasma in a direct-current magnetron sputtering system. The target was a 99.995% pure zinc disk of 5-cm diameter from Williams Advanced Materials. Various amount of vanadium stripes (Materials Research Corporation—Marz grade—99.99% purity) of about 0.15-cm width were fixed diagonally on the target for the purpose of co-sputtering. The experimental conditions were as follows: The distance between the target and the substrate was 3 cm. The initial pressure in the vacuum chamber was 5×10^{-5} Pa. Oxygen gas was introduced through a leak valve up to a pressure=0.1 Pa, and then argon gas was introduced. The total (Ar+O₂) pressure during sputtering was 10 Pa. The high voltage was 850 V and the current was 50 mA. Up to $x=15\%$ V-doped samples were obtained by co-sputtering zinc and vanadium. The film composition was estimated by X-ray Photoemission Spectroscopy.

The XANES measurements were performed on beamline 9.3.2 at the Advanced Light Source in Lawrence Berkeley National Laboratory. High-resolution XANES spectra were taken in the V L_{2,3}, O K, and Zn L₃ absorption edge regions, while the monochromator was set at a resolving power of ≥ 4000 . The photon flux at the sample was about 10^{11} photons/

* Corresponding author.

s/0.1% BW. The base pressure in the experimental chamber was about 2×10^{-8} Pa. XANES measurements were performed in total electron yield mode by measuring sample current. The beam flux (I_0) signal from a gold grid was used to normalize the spectra.

3. Results and discussion

Fig. 1 shows room-temperature XANES data of vanadium-doped ZnO thin films at the V $L_{2,3}$ and O K edge region as a function of vanadium doping. The energy scale was calibrated using absorption peaks of Cr $L_{2,3}$ edges originated from the coatings of monochromator [5]. We normalized the spectra by subtracting a straight line fitted to the region before the peaks (below 512 eV), and adjusting the intensity of the spectra to 1 at 548 eV.

V $L_{2,3}$ edge region shows a well-resolved prepeak at about 515.5 eV in addition to the L_3 and L_2 edges at about 517.7, and 524.7 eV, respectively. The prepeak is a signature of electron transition from V 2p into the unoccupied V 4s states [6]. Since the 4s states are full in elemental vanadium, the observation of the prepeak implies that V is not in the elemental form in the film down to the detection limit of XANES. In other words, there is no detectable metallic clustering of V atoms in the film. The L_3 and L_2 edges are due to electron transition from $2p_{3/2}$ and $2p_{1/2}$ energy levels to V 3d–O 2p hybridized bands. The decrease in the apparent spin–orbit splitting of V 2p level in the absorption spectra (~ 7.0 eV) as compared to the splitting observed in XPS (~ 7.7 eV) is a natural consequence of the strong interaction between the 2p core hole and the 3d electrons in the final state [7,8]. These interactions are of the same order of magnitude of the V 2p spin–orbit splitting which causes a large redistribution of the intensity throughout the entire spectra [8]. There is no significant shift in the peak positions as a function of V doping. This observation suggests that the oxidation state of V in the films remains the same. The peak position of L_3 edge suggests that V is in +4 oxidation state in the film [9]. The peak-intensity

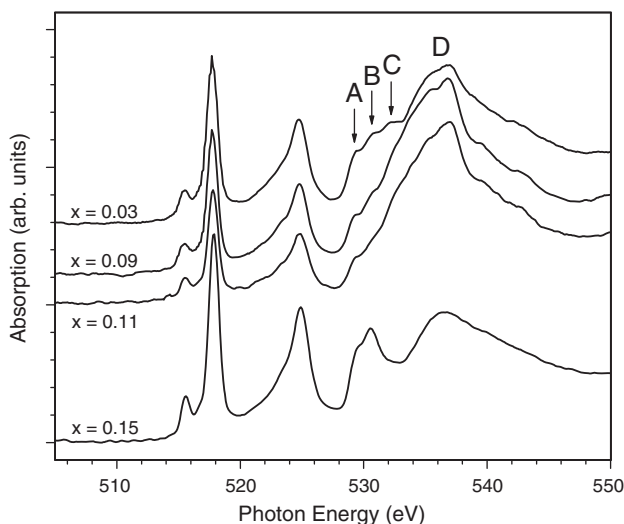


Fig. 1. Room-temperature XANES data of vanadium-doped ZnO thin films at the V $L_{2,3}$ and O K edge regions as a function of vanadium doping.

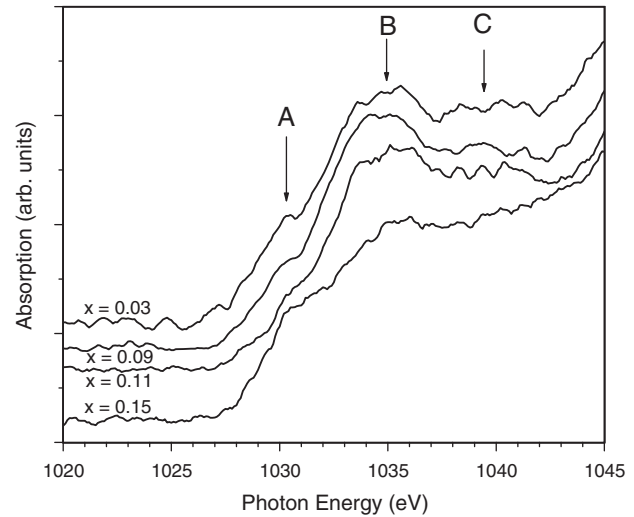


Fig. 2. Room-temperature XANES data of vanadium-doped ZnO thin films at the Zn L_3 edge region as a function of vanadium doping.

ratio $I(L_3)/I(L_2)$ is about 2, also indicating +4 oxidation state of V in the film [10]. Since covalency reduces the number of filled states with O 2p character, the intensity of the peaks is a measure of covalency strength; the higher the intensity the higher the covalency [11]. Note that the peak intensity decreases slightly as x varies from 0.03 to 0.11 and then markedly increased at $x=0.15$. This may be due to the formation of a secondary phase at $x=0.15$. In fact, the solubility limit of V in ZnO is about 5 mol%, which is equivalent to $x \sim 0.1$. At higher V concentrations, precipitation of VO_2 phase occurs [12].

O K edge region shows three peaks labeled A, B, and C at about 529.4, 530.8, and 532.3 eV, respectively in addition to a broad peak (labeled D) centered about 536.3 eV. Peaks A, B, and C are due to transitions from O 1s to the V 3d–O 2p and Zn 4d–O 2p hybridized bands while Peak D is assigned to V 4sp–O 2p hybridized bands [7,11]. Only Peak D is observed in pure wurtzite ZnO [13]. Ishida et al. [3] assigned Peaks A, B, and C to π^* , $d_{//}$, and σ^* bands, respectively based on molecular-orbital and crystal-field ideas. It is interesting to note that the Peak-C intensity gradually decreases as V-content increases and finally disappears at $x=0.15$. We believe that V in +4 oxidation state acts as electron donor and fills the σ^* band [11]. In fact, Cao et al. [14] have observed in their XPS study of Al and Mn codoped ZnO films that Al^{3+} and Mn^{4+} act as electron donors. Defects can also have considerable influence on XANES spectra as they distort the local symmetry and hence affect the amount of hybridization. A detailed discussion of O K edge features would require a symmetry-projected band structure calculation, which is not available at present. Ishida et al. [3] have observed in $Zn_{0.95}V_{0.05}O$, using photoemission spectroscopy, hybridization of O 2p band with V 3d band that forms in the band gap region of ZnO. However, they have also observed suppression of spectral weight at the Fermi level, indicating on-site Coulomb repulsion of V 3d electrons.

Fig. 2 shows room-temperature XANES data of vanadium-doped ZnO thin films at the Zn L_3 edge region as a function of vanadium doping. We normalized the spectra by subtracting a

straight line fitted to the region before the peaks (below 1025 eV), and adjusting the intensity of the spectra to 1 at 1098 eV. The prepeak A at 1030.4 eV is a signature of electron transition from Zn 2p into the unoccupied Zn 4s states [15]. Peaks B and C centered about 1035 and 1039.5 eV, respectively are attributed to the Zn 4d(t_{2g})-O 2p and Zn 4d(e_g)-O 2p hybridized bands [15]. This is in excellent agreement with the experimental and calculated spectra of w-ZnO [13,15,16], suggesting 4-fold coordination of Zn in the film. Note that the spectral weight at Peak C decreases as V content increases and finally disappears at the highest V doping ($x=0.15$). Similar observation was noted, in Fig. 1, with Peak C of O K edge spectra. This correlation seems to provide additional confirmation for the hybridization of Zn 4d and O 2p bands. We suggest that the disappearance of Peak C at $x=0.15$ in both spectra is due to the formation of a secondary phase, possibly VO₂ [12].

4. Conclusion

XANES technique has been used to investigate the electronic and atomic structure of vanadium-doped ZnO thin films obtained by reactive plasma. V L_{2,3} edge spectra show no sign of metallic clustering of V atoms in the films and indicate a secondary phase (possibly VO₂) formation at $x=0.15$. The peak positions and the peak intensity ratios suggest that the oxidation state of V in the films is +4. O K edge spectra suggest that V⁴⁺ acts as electron donor and fills the σ^* band. Zn L₃ edge spectra indicate that Zn in the films is in 4-fold coordination like that in pure wurtzite ZnO.

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