X-RAY PHOTOELECTRON SPECTROSCOPIC (XPS) INVESTIGATION OF INTERFACE DIFFUSION OF ZnO/Cu/ZnO MULTILAYER

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The multilayer of ZnO/Cu/ZnO was prepared by Rf sputtering. X-ray photoelectron spectroscopy analysis has been performed to study the chemical states of the core level atoms. Inter layer diffusion has an importance in the multilayer structure for different applications such as conductivity so we studied the possibility of diffusion of interlayer of the Cu(I) . Evidence for the presence of Cu(II) oxidation state has been obtained from the shakeup satellite structure of $Cu2_p$ core level atoms. The deconvolution of O 1_s was found to associate with the C bond. The chemical state of Zn2p was performed to study the bonding of Zn-O core level atoms.

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1. Introduction

ZnO is a promising material due to its excitation energy, meting point and high stability [1]. ZnO thin films have a various application in piezoelectric [2], integrated optic [3], gas sensitive devices and transparent conductive oxide [4]. The properties of ZnO thin films have been modified by addition of dopants and post annealing process [5]. Recently, the combination of semiconductor material and the metals in the forms of multilayers are used to enhance the properties of ZnO thin films such as conductivity, piezoelectric applications [6].

Metal oxide-metal-metal oxide multilayer thin films have been investigation to increase the various properties such as conductivity without disturbing the some basics and important properties like transmittance [7,8]. The copper metal has been used to increase the properties of ZnO in form of transmittance and conductivity [9]. However, there is a lack of investigations about the interface and diffusion of metal in the metal oxide multilayer thin films.

X-ray photoelectron spectroscopy (XPS) also known as electron spectroscopy for chemical analysis (ESCA) is used to study the surface composition of material as well as the in depth and interface of the multilayer thin films [10]. XPS uses a monoenergetic X-ray source to irradiate the surface of the material under high vacuum. The emitted electrons are analyzed with respect to their binding energy. XPS also provides the detailed information about the chemical state of the particular atom. The change in the chemical shift of the atom with different bonding configurations are known as chemical state of the particular atom [11]. XPS is also used to study interface diffusion, catalysts [12,13], polycrystalline compounds [14,15] and superconductor [16,17].

According to the best of our knowledge there are very few articles on the XPS interface of multilayer. In this research article, we focused the complete XPS study of Zinc Oxide-Copper - Zinc Oxide (ZnO/Cu/ZnO) multilayer and the possible interface of Cu layer. We analyzed the

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surface composition of the upper layer, the chemical state of the surface atoms, interface of Cu metal and depth profile of the multilayer of ZnO/Cu/ZnO.

2. Experimental Procedure

The multilayer ZnO/Cu/ZnO was prepared by using the radio frequency (RF) magnetron sputtering (DC/RF Magnetron Sputter System, Syskey Technologies, Taiwan) technique. High purity target (99.999%) of ZnO (3 × 0.6 inch) and Cu (3 × 0.6 inch) was used to deposit the multilayer. The plasma was generated inside the chamber using argon gas with flow rate 20 sccm at RF power of 200 watt for the ZnO target and 100 watt for Cu target while the base pressure, operating pressure, substrate rotation and target–substrate distance were adjusted at 1×10^{-6}, 5×10^{-3} Torr, 15 rpm and 14 cm respectively. To prepare the first layer of ZnO thin film the deposition time was fixed at 600 sec to produce film thickness 50 nm. The inter layer of Cu was deposited by fixing the time at 100 second to prepare the Cu layer of thickness about 20 nm. Finally, the upper layer of ZnO thin film was prepared by fixing the deposition time at 600 sec to deposit the film thickness of 50 nm.

2.1 Characterizations

The surface profiler (DektakXT, Bruker, Germany) was used to measure the films thickness. XPS (PHI 5000 Versa Probe II) having monochromatic X-ray source of Al-Kα (hν = 1486.6 eV) with spot size of 200 µm has been used. The analyzer of 187.85 eV was used while having the power of 50 W. The argon ion was used to clean the upper surface as well as to analyze the interface and depth profiling of ZnO/Cu/ZnO multilayer.

Multipack Software (VERSION 9, ULVAC-PHI, Inc. Japan) was used to analyze the XPS data and for the fitting of Gaussian-Lorentzian line shapes, effects of spin-orbit splitting, surface composition, interface and depth analysis of ZnO/Cu/ZnO multilayer.

3. Results and discussion

3.1 Surface analysis

Most elements occurring in the nature have photoelectron peak from 0 to 1100 eV. So the range of XPS survey scan was kept from 0-1100 eV in order to find the surface composition of upper layer of ZnO/Cu/ZnO XPS. Fig.1. shows the elemental composition of the upper layer of ZnO/Cu/ZnO and the Cu interface layer. In addition to Zn and Oxygen peaks we also observed some carbon peaks on the upper surface of the multilayer. . The presence of carbon peaks was considered the contamination which arose during the transfer of sample from RF to XPS chamber [18,19]. The upper surface was then etched with argon ion to remove the surface contamination.

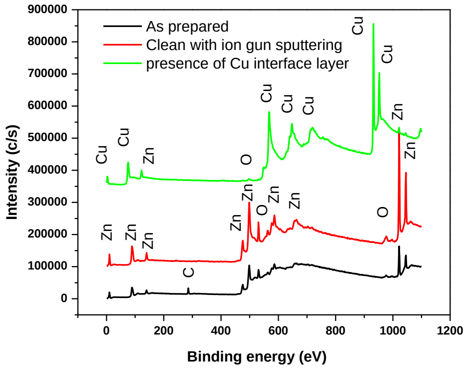


Fig.1. Elemental surface composition of upper layer of ZnO/Cu/ZnO

3.2 Chemical state

3.2.1 Zinc

The Zn $2p_{3/2}$ spectrum of Zn oxide is shown in Fig.2.

For transition metals,. It has been noted that the binding energy of surface atoms is found to be different from the bulk atoms due to a reduction in coordination number of the surface atoms [20] So, The binding energy of Zn $2p_{3/2}$ surface atoms in our case has been found 0.1 eV different from bulk atom which is also agreed with the reported data [21].

Zn $2p_{3/2}$ peak was found at 1022.10 eV which is the formation of Zn-O bond. Johan et al [22] also confirm the photoelectron emission of Zn $2p3_{/2}$ at 1022 eV. Espinos et al [23] and Gao et al [24] reported the change in binding energy of Zn photo electron and auger parameter of metal thin films at nanoscale.

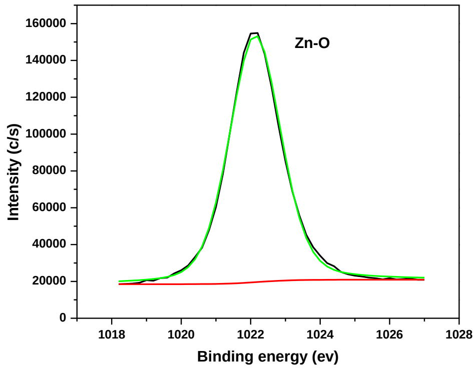


Fig.2. Zn $2p_{3/2}$ spectra of ZnO/Cu/ZnO multilayer

3.2.2 Oxygen

The asymmetric peak of O_{Is} is shown in Fig.3. The peak was deconvoluted by using gauss-lorentz fitting. The peak was found at 530.94 eV and 532.74 eV. The peak at 530.94 eV is considering as a metal oxide *i.e.,* Zn-O bond. According to Biesinger et al [25], the second peak in metal oxide with higher binding energy can be ascribed as a defect in the surface. The presence of peak at 532.74 eV shows the defect in the metal oxide which is the confirmation of O-C bond. Jessica et al [26] also observed the O-C bond at 532.7 eV. In the survey scan of upper surface of ZnO/Cu/ZnO also confirm the presence of carbon contamination. This might be absorbed on the upper layer of ZnO/Cu/ZnO during the shifting of sample from RF chamber to XPS chamber.

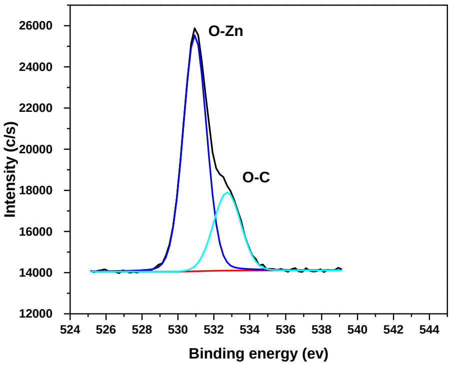
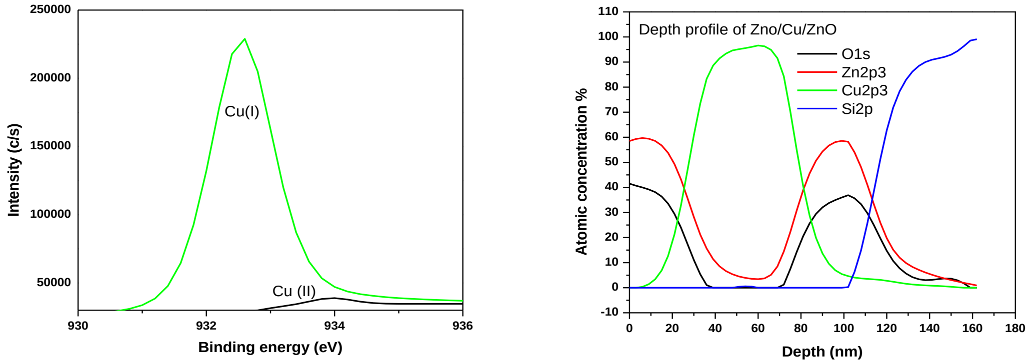


Fig (3) XPS spectra of core level O Is with deconvoluted peaks

3.2.3 Copper

In order to find the ratio of valence state of copper in the multilayer ZnO/Cu/ZnO, it is important to analyze the Cu $2p_{3/2}$ transition of the copper content in the ZnO multilayer.Fig.4.

shows the deconvolution of the Cu $2p_{3/2}$ peak positions and depth profile of ZnO/Cu/ZnO multilayer to estimate the chemical state of the Cu(I). We have observed the shakeup satellite in the interface of ZnO/Cu/ZnO multilayer. Shakeup satellites are produced due to the interaction of outgoing photoelectron with the valance electron. The binding energy of the shakeup satellite is always higher on the calculated binding energy scale [27]. One peak was found at 932.55 eV which was evidence of Cu(I) [28].The shakeup satellite was found at 933.95 eV that considered the formation of Cu (II). The Cu(I) was found 98.55% whereas Cu(II) was 1.45 % in the chemical state of Cu $2p_{3/2}$. Poulston et. Al [29] and Wang et. Al [30] also found the shakeup line in Cu $2p_{3/2}$ spectra which indicates the presence of Cu(II).



Fig(4).Cu $2p_{3/2}$ spectra of the copper interface layer and depth profile of ZnO/Cu/ZnO multilayer.

4. Conclusion

The survey scan of the upper layer of ZnO/Cu/ZnO shows the Zn enriches thin film. The atomic concentration of zinc and oxygen was found 56.2% and 43.8% respectively. The O 1_s spectrum shows the bridging of core level atoms with Zn in the upper layer of ZnO/Cu/ZnO. The interface diffusion of Cu(I) thin film in ZnO/Cu/ZnO multilayer showed through depth profiling. The concentration of Cu(I) and Cu(II) can be calculated by fitting the $Cu2_p$ core level atom. The presences of shakeup satellite peak confirmed the interface diffusion of Cu(I) and the concentration of Cu(I) and Cu(II) was found about 98.55% and 1.45 % respectively. The information about the interface diffusion of thin layer in the multilayer structures can be useful for their different potential applications such as to enhance the conductivity of metal oxide-metal-metal oxide thin films. So, XPS is very suitable and attractive tool for in situ study of surface atoms, chemical state and interface diffusion of multi-layer thin films. Therefore, this method is a key point to study the quality of the interface diffusion of multilayer thin films which is crucial for the enactment of advanced materials, optoelectronic devices, sensor, etc

Conflicts of Interest

The author has mention all the relevant members and funding agencies involved in this research work.

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