

SEM/XPS/XRD Study of Zinc oxidation

N. TABET ⁽¹⁾, M. FAIZ ⁽¹⁾ and A.L. OTEIBI ⁽²⁾

⁽¹⁾ Surface Science Laboratory, Physics Department, KFUPM, Saudi Arabia.

⁽²⁾ Physics Department, College of Girls, Dammam, Saudi Arabia

Email: natabet@kfupm.edu.sa

ABSTRACT. We have studied the growth of oxide layers obtained by dry oxidation of pure Zinc substrates, under air, at different temperatures. Both Zinc polycrystalline foils and pure Zn single crystals were considered. X-ray photoelectron Spectroscopy (XPS) has been used to monitor the growth of the oxide after successive treatments. Furthermore, Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) were used to study the microstructure and composition of the oxide layers. The results showed the formation of textured oxide layers on Zn single crystal substrates. The ZnO crystallites have a preferential orientation normal to (0001) surface of the substrate. Above the melting point, the microscopic observations revealed the formation of a high density of ZnO nanofibers.

1. Introduction

Zinc Oxide (ZnO) is an important material of growing interest because of its use in a wide range of applications. It has good conductivity and transparency in the visible light range in addition to its low cost. These characteristics allow zinc oxide to compete with doped tin oxide and Indium-Tin-Oxides (ITO). In addition, ZnO can be used in a wide variety of technological applications such as gas sensor devices (Kwong *et al.* 1995), transparent electrodes (Major *et al.* 1986), (Kubon *et al.* 1994) and (Amlouk *et al.* 1994), piezoelectric devices (Ambia *et al.* 1992), and varistors (N. Tabet *et al.* 1994). Zinc oxide has recently gained a tremendous interest because of its wide direct gap ($E_g=3.37\text{eV}$) that makes it a strong candidate for the fabrication of blue Light Emitting Diodes (LEDs) and Laser Diodes (LDs) (Zu *et al.* 1997). Actually, ZnO is currently considered as the main competitor of another direct gap II-VI compound that is GaN ($E_g = 3.5\text{eV}$). The growth of a ZnO layer of controlled properties would be of a crucial importance towards the development of ZnO based devices. In this work, we have carried out oxidation experiments below and above the melting point of zinc ($t_m = 419^\circ\text{C}$). The microstructure of the oxide layer was characterized by many techniques including Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS) and X-ray Diffraction (XRD).

2. Experimental

2.1 Sample preparation and oxidation experiments

Pure Zn single crystals of 10 mm diameter and 3 mm thickness were mechanically polished using SiC paper then diamond paste. The polished surface was normal to [0001] direction of the crystal growth. We have also used polycrystalline Zinc foils of 1mm thickness. The surface of the foils were mechanically polished with SiC paper only and cleaned with acetone and rinsed with distilled water. Oxidation treatments of various durations were carried out under air at different temperatures between 400 °C and 500 °C.

2.2 Microstructure and composition characterization

The composition of the oxide layer was investigated by XPS while XRD and SEM were used to analyze its crystallinity and microstructure. The XPS electron Spectrometer was of the type VG-ESCALAB MKII. The X-ray source was an Aluminum anode ($K\alpha$, 1486.6eV). The incident beam was not monochromatized. The energy resolution of the Spectrometer was about 1 eV. Zn2p, Zn3d, ZnLMM Auger, O1s and C1s lines were systematically recorded. The charge shift correction of the binding energies was done by using, as a reference, the C1s line ($E_b = 284.6\text{eV}$) stemming from the contamination layer. Quantitative analyses were performed by using a dedicated software (ECLIPSE) that takes into account the characteristics of the instrument as well as the sensitivity factors of the elements.

1. Results and Discussion

3.1 XPS spectra

XPS analyses of the samples were carried out before and after oxidation. Figure 1 shows the O1s line recorded after successive oxidation treatments of Zinc single crystal for various durations at $T = 400\text{ }^\circ\text{C}$. The main peak at 530 eV binding energy corresponds to the oxygen atoms bound to Zn in ZnO. The shoulder observed at 532 eV has been assigned by many authors to the presence of water as its binding energy lies between 531.5eV (OH) and 533eV (H₂O), (Avalle 1992) and (Meng 1994).

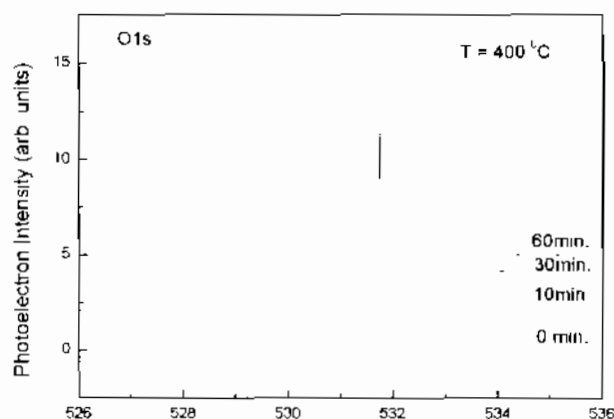


Fig. 1: O1s line after oxidation of Zn single crystal at $T=400\text{ }^\circ\text{C}$.

Zn2p and Zn3d lines were also recorded but no measurable change in their respective binding energies was observed because the value of the chemical shift resulting from the oxidation of the Zn atoms is much lower than the energy resolution of our electron spectrometer (1eV).

3.2 SEM characterization

Figures 2 a, b show secondary electrons SEM micrographs of the surface of two single crystals after oxidation treatments under air, at $T=400^{\circ}\text{C}$, for 24 hours and 9 days respectively. The inset in Fig.2 b shows the microstructure of the oxide layer at high magnification ($\times 3000$).

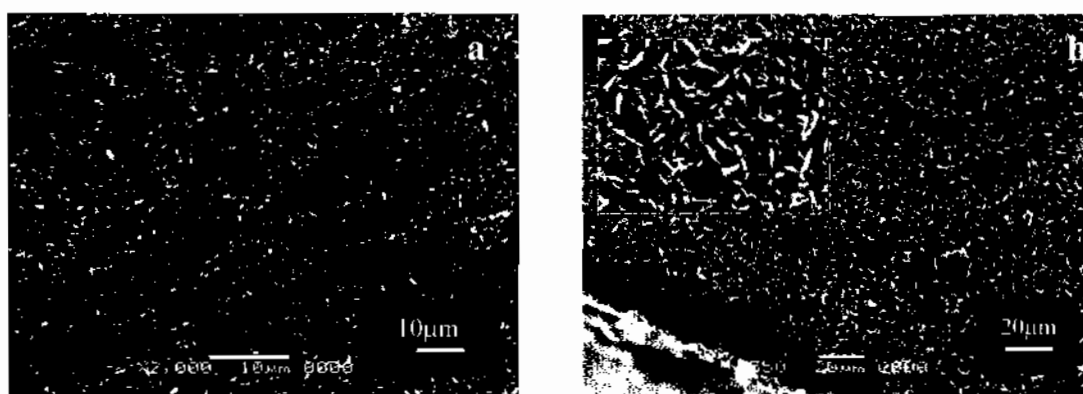


Fig. 2: SEM image of the surface of Zn single crystals after oxidation, $T=400^{\circ}\text{C}$, 24 hours (a) and 9 days (b).

Fig. 3 a, b, and c show the microstructure of polycrystalline foils after oxidation at $T=400^{\circ}\text{C}$, and 500°C . One can clearly notice the presence of a high density of nanofibers of zinc oxide in Fig.2 b and c corresponding to oxidation treatments carried out above the melting point of Zinc.



Fig. 3: SEM images of Zn foil after oxidation at $T=400^{\circ}\text{C}$, 7h (a), $T=450^{\circ}\text{C}$, 19h, (b) and $T=500^{\circ}\text{C}$, 6h, (c)

Actually, a close look at Fig. 3 a reveals also the presence of a smaller density of nanorods of zinc oxide.

We have reported on Fig. 4 the XRD spectra obtained from Zn foils oxidized at $T=500^{\circ}\text{C}$ for 6h and Zinc single crystal oxidized at $T=400^{\circ}\text{C}$ for 24h. We have also included the spectra of a non-oxidized foil of pure zinc and that of a ZnO powder as references. The XRD experiments were performed using the $\text{CuK}\alpha$ line ($\lambda = 1.5418\text{\AA}$). One can notice the presence of Zinc peaks after 6h treatment at $T=500^{\circ}\text{C}$ indicating that the 1mm foil was not completely oxidized. In addition, the lines are broader than those of the ZnO powder. This broadening is related to the presence of the nanofibers on the surface of the foil. It is worth pointing out the presence of a strong peak (002) in the spectrum obtained from the surface of the oxidized single crystal. This suggests a preferential orientation of the ZnO crystallites along the direction (0001) perpendicular to the surface of zinc substrate.

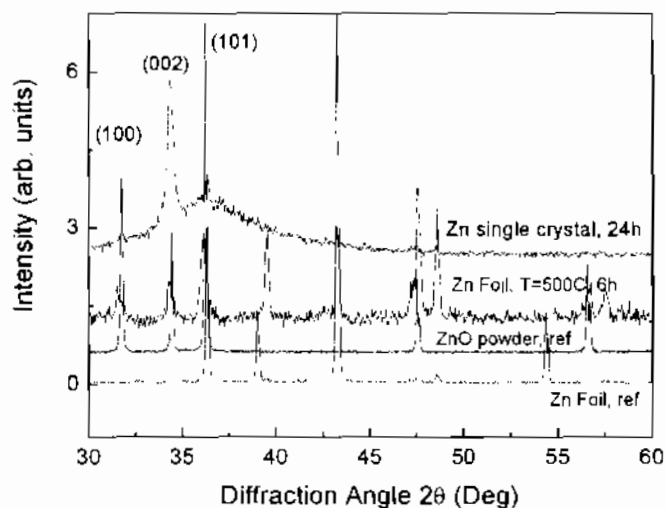


Fig. 4. XRD patterns of oxidized single crystals and polycrystalline foil.

4. Conclusion

We have investigated the oxidation of single crystals and polycrystalline foils of pure zinc. In the case of single crystals, the results revealed the formation of textured polycrystalline layers of ZnO crystallites with a preferential orientation perpendicular to the surface of the substrate. Above the melting point, the SEM observations revealed the formation of a high density of ZnO nanofibers.

Acknowledgments

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دراسة أكسيد الزنك بالمجهر الإلكتروني الماسح ومطيافية الإلكترونات الضوئية السينية

نوار ثابت^(١) محمد فايز^(١) وأمل ل. العتيبي^(٢)

^(١) مختبر علم السطوح، قسم الفيزياء، جامعة الملك فهد للبترول والمعادن

الظهران، المملكة العربية السعودية

^(٢) كلية البنات، الدمام، المملكة العربية السعودية

المستخلص. درس أكسيد الزنك بشكل واسع في الماضي لما له من خواص كهربائية و ضوئية يمكن استخدامها في العديد من التطبيقات التقنية المختلفة مثل أجهزة الغاز الحساسة، الإكترودات الشفافة، الأجهزة الكهروضغطية وكذلك المقاومات المتغيرة. حديثاً ظهر أكسيد الزنك كمادة ضرورية لتصنيع دايود الانبعاث الضوئي. قمنا بدراسة نمو طبقات الأكسيد الناتجة عن الأكسدة الجافة لطبقة تحتية من الزنك النقي عند درجات حرارة مختلفة. استعملنا عينات زنك بلورية وكذلك عينات على شكل رقائق متعددة البلورات. استخدمت تقنية مطيافية الإلكترونات الضوئية السينية لمتابعة نمو الأكسيد في المراحل الأولى من عملية الأكسدة. قمنا أيضاً بدراسة أكسدة عينات تم زرع عنصر النيتروجين فيها بطاقة 3 keV باستعمال قاذف أيوني ملحق بجهاز الطيف الإلكتروني. وتم متابعة جرعة النيتروجين المزروع عن طريق تسجيل إشارة النيتروجين في الطيف الإلكتروني بعد دورات زرع متتالية. كذلك استخدم المجهر الإلكتروني الماسح ومطيافية تبدد الطاقة والحيود السيني لمعاينة البنية المجهرية والتركيب الكيميائي لطبقة الأكسيد. أظهرت النتائج حركية تأكسد بطيئة وتكون ألياف أكسيد الزنك نانومترية على سطح العينات المعالجة عند درجات حرارة عالية.