

Atmospheric dielectric barrier discharge plasma synthesis of nanoporous zinc oxide films using zinc acetylacetonate hydrate as precursor

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Abstract: Nanoporous ZnO films were prepared at room temperature using atmospheric dielectric barrier discharge (DBD) plasma. Surface morphology and chemical composition were investigated by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The presence of zinc and oxygen in the film was verified by the XPS spectra and a nanoporous structuration of the films was suggested by the SEM images.

Keywords: atmospheric plasma, dielectric barrier discharge, ZnO films

1. Introduction

Zinc oxide (ZnO) has received substantial interest in recent years due to its transparent and conductive properties and has been regarded as a promising candidate for indium tin oxide (ITO) replacement [1]. Nanostructured ZnO thin films show some attractive performances such as high catalytic efficiency, excellent thermoelectric properties and oxygen storage capability [2, 3]. Consequently, nanostructured ZnO has been deemed to be a potential material for the preparation of electrochemical devices [2]. Many different techniques such as sol-gel chemical process [3], atmospheric plasma [4] and chemical vapour synthesis [2, 5] have been used for the synthesis of ZnO films. Compared to other techniques, atmospheric dielectric barrier discharge (DBD) has the advantages of excellent applicability for large-scale production and low cost. Therefore, it could present a significant interest in the synthesis of nanoporous ZnO films.

In the present work, atmospheric DBD is used for the preparation of ZnO thin films. Zinc acetylacetonate hydrate is chosen as precursor because of its non-toxic and non-flammable properties. The morphology, chemical composition and thickness of the as-prepared coatings were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and profilometry, respectively.

2. Experimental

A scheme of the atmospheric DBD system is presented in Fig. 1. The plasma was fed with argon (Ar) and oxygen (O₂). Their flow rates are of 2.0 L/min and 0.1 L/min, respectively. Zinc acetylacetonate hydrate powder (Zn(C₅H₇O₂)₂·H₂O), provided by Sigma-Aldrich Corp., is placed in a bubbler and heated at 403 K. A 0.2 L/min Ar gas flow is used to carry the precursor vapours. The wire connecting the chamber and the bubbler is heated at 373 K and the discharge power is set at 30W. The

distance between the two electrodes is fixed at 10 mm and the substrate is placed on the bottom electrode. Prior to the deposition, the chamber is pumped down to a pressure of 2.3 Torr in order to reduce atmospheric contaminations. The atmospheric pressure is achieved by the injection of Ar gas. The deposition duration is 5 minutes.

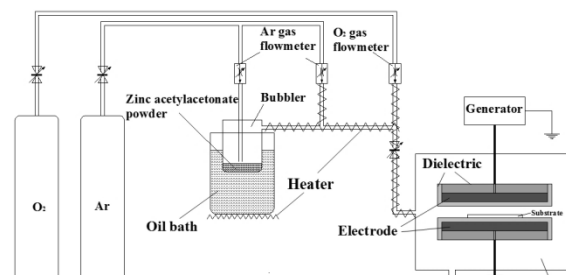


Fig. 1. Scheme of the atmospheric DBD system

3. Results

ZnO thin films are deposited on silicon wafer by atmospheric DBD system at room temperature. An average thickness of 300 nm is measured by profilometry and the deposition rate is up to 60 nm/min.

Fig.2 illustrates XPS spectra of zinc acetylacetonate hydrate powder and ZnO coatings synthesized on the glass, respectively. The concentration of O 1s increases from 31.33% to 46.95% as a result of atmospheric dielectric barrier discharge synthesis. On the contrary, the Zn 2p_{3/2} concentration is reduced from 10.65% to 3.94% and the C 1s concentration varies from 58.02% to 49.11%. These variations are mainly linked to the destruction of the organic part of the precursor in the plasma. Fig.3 presents the C 1s high resolution XPS spectra of the precursor powder (a) and of the coating synthesized on glass substrate (b). A significant difference in the proportion of the different components of the

carbon is observed. This indicates that the plasma favours the formation of C=O and O-C=O bonds at 287.9 eV and 289.2 eV respectively. On the other hand, the intensity of C-C/C-H peak centred at 284.9 eV is decreased. This could be explained by the presence of oxygen in the plasma. Indeed, it is well known that oxygen radicals and metastables are responsible of the degradation and oxidation of organic substances [6].

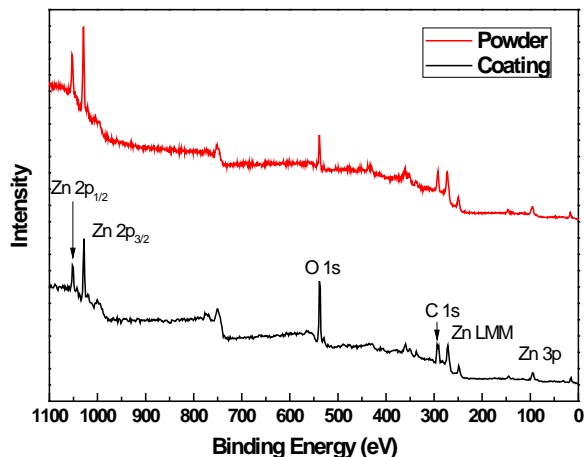


Fig. 2. XPS spectra of zinc acetylacetonate hydrate powder and ZnO coating synthesized on glass substrate

The Zn 2p XPS high resolution spectra of the precursor powder (a) and the coating (b) are shown in Fig.4. For the precursor powder, Zn 2p_{3/2} peaks is located at 1021.2 eV and the gap between the positions of Zn 2p_{3/2} peaks and Zn 2p_{1/2} peaks is 23.13 eV, whereas, the corresponding values of the synthesized coating are 1022.1 eV and 23.11 eV, respectively. The shift in the binding energy of Zn 2p_{3/2} peak is probably ascribed to the rearrangement of Zn-O bonding in the plasma and the morphologic difference between the zinc acetylacetonate powder and coating shown in Fig.5 [7, 8].

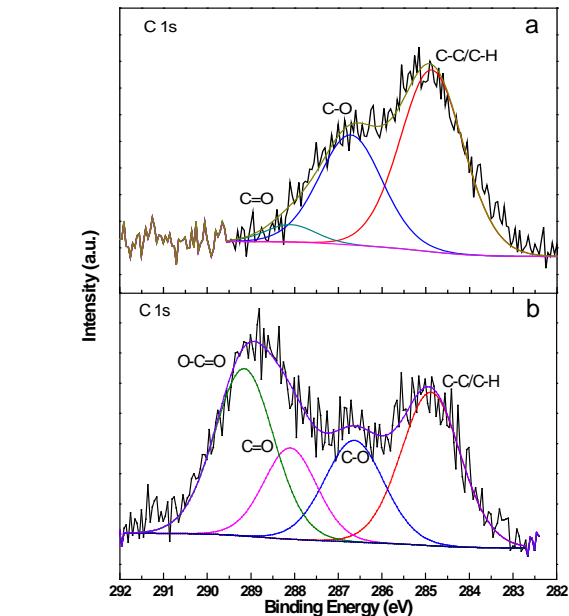


Fig. 3. C 1s high resolution XPS spectra of the precursor powder (a) and the coating (b)

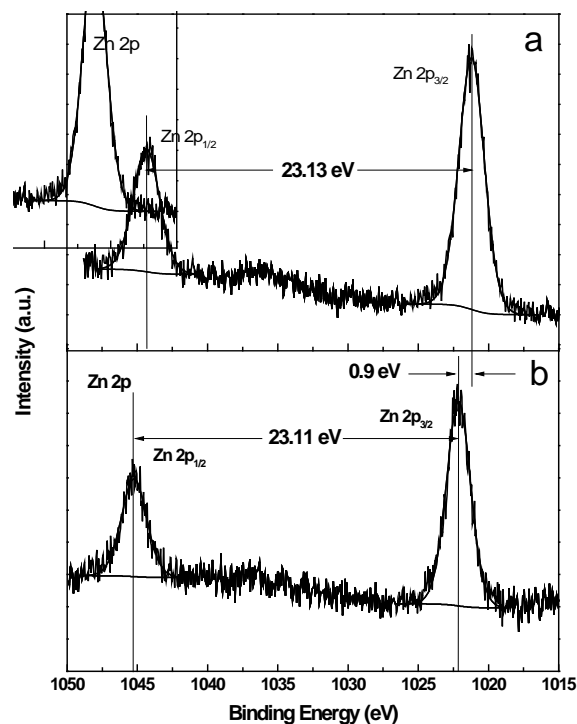


Fig. 4. Zn 2p XPS high resolution spectra of precursor powder (a) and coating (b)

The morphology of ZnO film synthesized on silicon wafer is presented in Fig. 5. The SEM image shows a porous structure which is probably due to the filamentary discharge and the nucleation and growth of the ZnO nanoparticles in the plasma phase [9].

The profilometry analysis allows the determination of a 60nm/min deposition rate which leads to a 300 nm average thickness of the coatings.

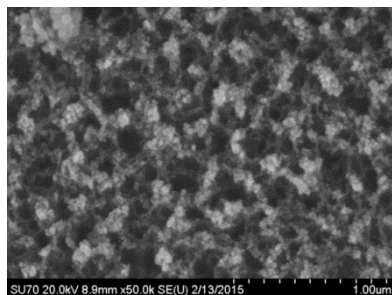


Fig. 5. SEM image of the ZnO film synthesized on silicon wafer

In summary, nanoporous ZnO thin films were successfully prepared at room temperature by atmospheric DBD plasma using zinc acetylacetonate hydrate as precursor. The XPS spectra analysis presented the differences of chemical composition between the zinc acetylacetonate hydrate powder and the ZnO coating. The SEM image suggested a porous structuration of ZnO coating.

4. Acknowledgment

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5. References

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