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Fabrication of Multilayer $ZnO/TiO_2/ZnO$ Thin Films with Enhancement of Optical Properties by Atomic Layer Deposition (ALD)

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Abstract. Atomic layer deposition (ALD) is a precision growth technique that is able to deposit either amorphous or epitaxial layer on a wide range of substrates. Multilayer thin films have been widely studied because their properties are different from those of bulk materials constituents owing to the two-dimensional films and high density of interfaces. Multilayer nanostructured thin films were fabricated on silicon and glass substrates by ALD. The optical and electrical of multilayer $ZnO/TiO_2/ZnO$ films were investigated. The microstructure compositions and surface morphology of these multilayer films were analyzed by X-ray diffraction (XRD), Atomic force microscope (AFM) and Scanning electron microscope (SEM). The optical properties were characterized using photoluminescence (PL) and UV-VIS spectroscopy. XRD patterns confirmed that ZnO with wutrtize crystal structure and TiO_2 with anatase structure were presented. The degree of crystallinity of multilayer thin films has been improved through the deposition of ZnO. The intensity of UV luminescence of the multilayer has increased as compared to the single layer TiO_2 and bilayer ZnO/TiO_2. The multilayer $ZnO/TiO_2/ZnO$ has high transmittance (above 80%) in visible region. All the result suggested that the use of multilayer thin films effectively enhanced the quality of films crystallinity and optical properties as compared to single layer ZnO and bilayer ZnO/TiO_2.

Introduction

Multilayer thin films consist of alternating layer of two different materials which may contain several repeated thin films layer in range of nano or micro scale [1] . Zinc Oxide (ZnO) based nanostructured composites become more attractive when being simply assemble together with other metallic oxide[2].The growth of transparent conducting oxide (TCO) semiconductor is essential as expending needed for transparent electrode for optoelectronic devices. ZnO thin films have wide applications due to the superior electrical [3-9] and optical properties [3-5, 7, 10, 11]. The outside layer can be deposited on the ZnO surface by different deposition method such as electron beam evaporation [12], sputtering system [13], and atomic layer deposition [14,15,16]. Titanium dioxide (TiO_2) is a ceramic material with versatile applications for self-cleaning, biocompatible, and corrosion resistance [17]. The unique microstructure and improved optical and electrical properties are reported [18-19]. The increase in light emission or efficiency enhancement for dye-sensitized solar cell definitely proves that these types of multilayer nanostructures or nanocomposite have enhanced optical and electrical properties that may have functional applications. The high precision and conformality of ALD process could produce bilayer thin films [15] and multilayer thin films with controlled thickness and microstructures. However, to the best of our knowledge, there is no report on multilayer of $ZnO/TiO_2/ZnO$ (ZTZ) thin films by ALD. In this paper we attempt to synthesize uniform multilayer of ZTZ thin films in order to obtain enhanced crystallinity and optical properties of this multilayer.

Experimental

ALD was used to deposit multilayer ZTZ on the silicon wafer and glass as substrate. ZnO was deposited at 280°C for 1200 deposition cycles. The process were operated with pulse H_2O at 0.15s and diethylzinc (DEZ) at 0.015s pulse rate, pumps at 5s, and nitrogen flow 20 sccm. The sequence of one ALD cycles was $H_2O/N_2/DEZ/N_2$. Then, TiO_2 thin films were deposited on ZnO films at 300°C for 2000 cycles. The process were operated with pulse H_2O at 0.15s and tetra-iso-propoxide (TTIP) at 0.20s pulse rate, pumps at 5s, and nitrogen flow 20 sccm. The sequence of one ALD cycle was $H_2O/N_2/TTIP/N_2$. After that, another ZnO layer was deposited at 280°C for 1000 cycles with same process parameters. The phase and crystallinity of the multilayer films were analysed by X-ray diffraction (XRD, Siemens Kristalloflex-D500) with Cu-Kα radiation. Eva software was used to analyse the phase. The surface morphology and surface roughness were characterized using Atomic Force Microscope (AFM, Veeco, CPPII-Research scanning probe microscope). ImageJ software was used to determine particle size from AFM image. The photoluminescence of the multilayer thin films were measured by Hitachi F-2500 fluorescence spectrometer. The optical transmittance spectra were measured by Biochrom Libra S33 UV/Vis-spectrometer.

Result and discussion

Uniform single layer, bilayer and multilayer thin films were deposited on silicon wafer substrates. Fig 1 shows XRD patterns of ZnO single layer, bilayer of ZnO/TiO_2 (ZT) and multilayer $ZnO/TiO_2/ZnO$ (ZTZ). All XRD patterns confirmed that ZnO with wutrtize crystal structure and TiO_2 with anatase structure were presented. XRD pattern of ZnO thin film matched with the wurtize structure (JCP 22.2CA 01-079-2205) and TiO_2 thin films matched with the anatase structure (JCPDS pattern 00-021-1272). All the peaks of the single layer ZnO deposited using 1200 cycles are in good accordance with the diffraction values of hexagonal wurtzite structure with predominantly (00.2) orientation. Bilayer ZT of thin films shows increases of intensity in orientation (0.02) after the deposition of TiO_2. Moreover, the intensity at (0.02) orientation increases for multilayer ZTZ. The sharp peak indicates the multilayer films are well crystallized. It shows that the films crystallinity has been drastically improved with multilayer deposition. The improvement of crystallinity of ZTZ multilayer thin films has also been reported using other techniques [20, 21]. The crystallite size calculated using Scherrer formula for ZnO, ZT, and ZTZ were 27.2 nm, 28.26 nm and 33.7 nm, respectively (Fig 2). The increase of crystallite size indicates that the crystallinity of ZTZ multilayer has been improved.

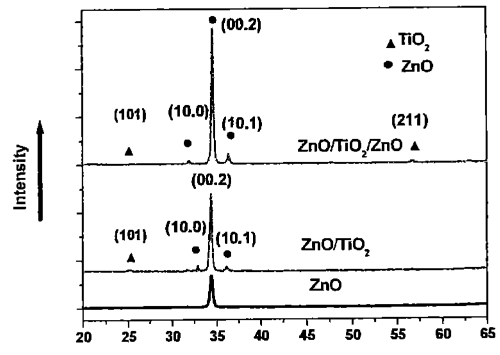


Figure 1: XRD pattern of ZnO, bilayer ZT and multilayer ZTZ thin films

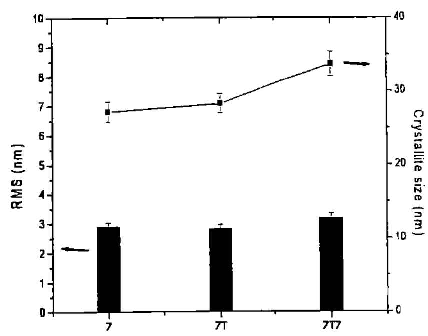
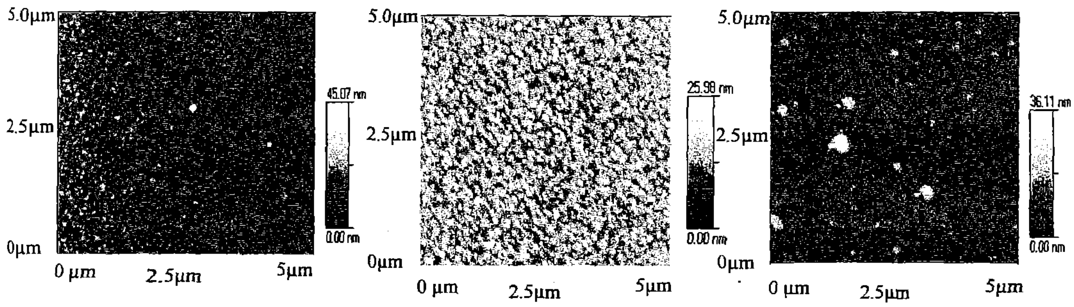


Figure 2: RMS and crystallite size of Z (ZnO),bilayer ZT,and multilayer ZTZ



(a) Single ZnO layer films (b) Bilayer ZnO/TiO_2 thin films (c) Multilayer $ZnO/TiO_2/ZnO$ thin films

Figure 3: AFM of single ZnO layer, ZT bilayer and ZTZ multilayer films

The morphology of thin films was observed with AFM, together with the assessment of the relative roughness of the thin films (RMS parameter). The morphology from AFM image (fig 3) illustrates that bilayer ZT consisted of compact grains which was very similar to the single ZnO layer. However, multilayer ZTZ had much larger grain size compared to the single layer and bilayer. The relative roughness of these thin films was also very close (fig 2). The value of RMS for ZnO, bilayer ZT and multilayer ZTZ were 2.89 nm, 2.80 nm and 3.17 nm, respectively. Particles sizes, orientation, shapes and distribution play an important role in governing the performance and reliability of polycrystalline films. An evolution of the particles size distribution may occur depended on the deposition temperature and impurities segregated at the grain boundaries [22]. The correlation between the films morphology and its optical properties is complicated. It is depends on grain size, orientation and grain boundaries. A grain boundary is identifying as the interface at which grains move towards and contact with another different crystal orientation. Several kinds of defect are present at grain boundaries such as dangling and impurities [23]. Therefore, multilayer thin films may attribute to the change of particle shapes that contributes to the improvement of crystallinity and optical properties. The crystallinity properties of the films is clearly dependent on the kinetics of arriving species at the surface [23].

The optical properties of thin films were the response of material deposited on the substrates to electromagnetic waves or light waves, principally in the wavelength spectrum of visible light (400-700nm). Figure 4 illustrates the transmittance spectra of ZnO thin films, ZT bilayer thin films and ZTZ multilayer thin films. It shows that multilayer ZTZ have high transmittance (~80%) in 450-800 nm range. However, there is a slightly decrease of ZnO thin films in 400-500nm range and slight increase of ZT bilayer in the range of 450 – 800 nm. Normally, transparent conducting oxide thins an exhibit a resistivity in the order of 10^{-3} cm or higher and average transmittance above 80% in visible range. The band energy (Eg) of ZnO, ZT and ZTZ was 3.31 eV, 3.34 eV and 3.35 eV, respectively. Choi [12] also reported the increase of band gap energy of multilayer $ZnO/TiO_2/ZnO$ prepared via electron beam evaporation. Since ZnO and TiO_2 materials have unlike band gaps, their combination should cover a broader light absorption spectrum than the single layer can cover [26]. The multilayer of two different materials show much improved and special optical properties because of the combination affect between the dissimilar materials as well as the enlarged the surface areas.

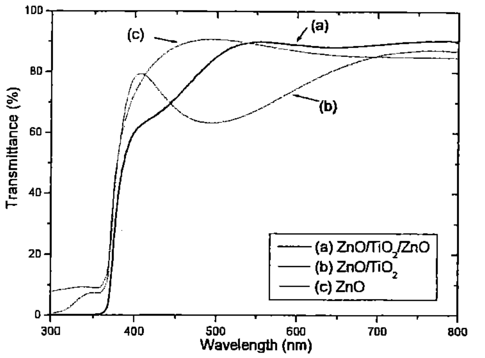


Figure 4: Transmittance of ZnO, bilayer ZT and ZTZ multilayer thin films

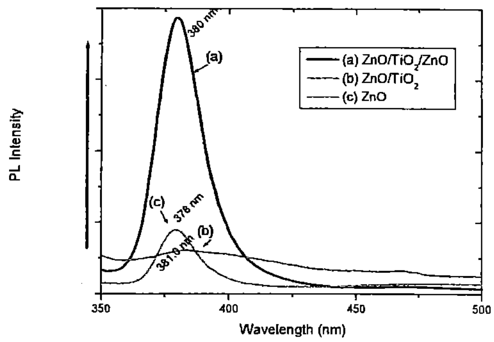


Figure 5: PL spectra of ZnO, bilayer Z/T and ZTZ multilayer thin films

Fig 5 shows the PL ZnO spectra, ZT bilayer and ZTZ multilayer thin films. The spectra were collected under photon excitation 320 nm using xenon lamp. The PL spectra shown strong and sharp UV emission located around 380 nm and no other visible light emission peak can be seen, demonstrated of good crystallinity quality of multilayer ZTZ thin films growth by ALD. The near UV emission is attributed to free-excition recombination [24]. Compared to the ZnO single layer, the UV emission of the multilayer ZTZ is greatly enhanced. The PL intensity of the UV emission increased with the increase of the crystallite size because of the enhanced crystallinity of thin film. This also may attributed to the higher barrier in valence band which prevents the hole movement [12]. These also agree with the particles size in multilayer. The enhanced the increase of UV emission can be explained with two reasons: the surface passivation effect due to the capping TiO_2 particles and the fluorescence resonance energy transfer (FRET) between TiO_2 layer and ZnO layer [19].

Conclusion

Uniform multilayer ZTZ thin films have been successfully deposited by ALD. The crystallinity of thin films has been improved with multilayer thin films. The intensity of UV luminescence of multilayer increases as compared to those of the single layer TiO_2 and bilayer ZT. It shown that multilayer ZTZ has high optical transmittance (above 80%) in visible region. It is suggested that the growth of multilayer ZTZ thin films enhanced the crystalinity and optical properties. The multilayer thin films show much enhanced the crystallinity and optical properties because of the combination and interaction effect between different metal oxides. These multilayer ZTZ thin films can be used to as transparent conductive thin films.

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