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Effects of gold nanoparticles on the growth of ZnO thin films and p-Si/ZnO heterostructures

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ABSTRACT

Gold nanoparticles (AuNPs) were grown on p-Si substrate in order to investigate its effects on the optical, electrical and structural characteristics of the electrochemically deposited ZnO thin films and produced p-Si/AuNP/n-ZnO hetero-structures. Homogenous distribution of AuNPs on p-Si substrate with an average size of 150 nm and surface plasmon resonance wavelength around 700 nm has been observed. Polycrystalline nature of ZnO thin films have been confirmed with the dominant crystal plane of (002) for the sample grown on bare p-Si substrate, while it is (100) plane dominant for the sample grown on the AuNPs/p-Si substrate. Formation of Zn-rich ZnO has been realized in ZnO thin films grown on the AuNPs substrate, while it is O-rich in the thin films grown on p-Si substrate with X-ray Photoelectron Spectroscopy. Enhancement of Raman peaks, near-bandedge and intra-bandgap absorption, and the near-bandedge emission has been observed on the ZnO thin films grown on AuNPs. Higher forward bias current values have been observed in the hetero-structure produced by interface AuNPs, p-Si/ AuNPs/n-ZnO.

1. Introduction

Metallic nanoparticles, such as Au and Ag, have recently attracted a lot of attention due to observed Surface Plasmon Resonance (SPR) effect in the visible region of the electromagnetic spectrum, that can be used to enhance materials' and devices' optical and electrical properties [1,2], besides their usage in many different biological applications such as in vivo cancer research [3]. The improvement in performance of the solid state devices such as photodetectors [4], solar cells [5], gas sensors [6], light emitting devices (LEDs) [7] and field effect transistors (FETs) [8] has been shown with either doping or decoration of the AuNPs on surfaces or interfaces of the devices. Solution based processed ZnO-Au photodetector was studied to understand the effect of how the AuNPs generate as high as 1.51×10^5 A/W responsivity [4]. Similarly, 2.6 times increased power conversion efficiency was realized in a Schottky-based graphene/Si solar cell by co-doping graphene with AuNPs [5]. Also, optically enhanced H_2 and CO gas sensor device was produced with AuNPs doped ZnO thin films [6]. On the other hand, AuNPs decorated on MoS_2 FET device was successful [8].

Using solution-based processing, AuNPs decorated devices have been widely used. Higher dye sensitized solar cell efficiency was achieved with AuNPs decoration on top of a ZnO nano-rod photo-electrode [9]. Only limited numbers of reports have been presented on the effects of the interface decoration of AuNPs on device performances and the material properties grown on top of NPs [10]. One of these studies, employed AuNPs embedded at the interface of the Al/AuNPs/SiC/Al Schottky diode show to improve current-density characteristics by modification of barrier height [10]. Similarly, light trapping at certain wavelengths and enhancement of current voltage characteristics were obtained in n-ZnO/AgNP/p-Si diode [11]. On the other hand, alongside the solid state device applications of AuNPs, it finds applications to enhance the photocatalytic activities [12,13].

One of the most important characteristics of AuNPs is tunability of the SPR frequency by the shape and size of the NPs [14,15]. Previously, we showed that average size and shape variation from 12 nm to 230 nm in size, from spherical to cuboid-like shape can be achieved by changing the parameters such as thickness of the Au film, thermal processing time and temperature [14]. In addition, the SPR frequency shift was observed from 520 nm to 750 nm. In this study, optical and structural effects of AuNPs, decorated on p-Si substrates, and on electrochemically grown ZnO thin films is presented in detail. Interface decoration effects on the AuNPs between ZnO thin films and the p-Si substrate has been investigated through p-Si/n-ZnO hetero-structure characteristics.

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2. Experimental

2.1. Synthesis of AuNPs

Experimental procedure to obtain the AuNPs is as follows: p-Si (100) substrates on which AuNPs were dewetted and then cleaned by RCA1 and RCA2 cleaning procedures. After the last step of RCA2 cleaning, SiO_2 layer was grown on Si by hot water oxidation (85 °C for 90 min). Then the oxide grown Si substrates were stored in a clean room ambient until Au film deposition. Before Au film deposition, the SiO_2 layer on the Si substrate was removed by HF dip (%1 in aqueous solution) for 30 s. Also, quartz substrates were put into the chamber in order to make the transmission measurements. After that, Au films were deposited on the Si substrate by evaporation at a pressure of 2×10^{-6} Torr by a growth rate of 2 Å/s. After 20 nm Au film deposition, samples were annealed at 600 °C for 90 min under N_2 atmosphere to induce NP formation.

2.2. ZnO thin film growth

After the AuNPs were formed onto the p-Si substrates, ZnO thin films were grown on the AuNP/p-Si substrates by electrochemical deposition (ECD). The deposition system, Gamry Referance 600 potentiostat/galvanostat, is a conventional three electrode cell with Au/p-Si substrate, Zn plate and Ag/AgCl electrodes, making up the working electrode, counter electrode and reference electrode, respectively. ZnO thin films deposition was performed in dimethyl sulfoxide (DMSO) solution. DMSO solutions were prepared in molarity of 0.1 M $LiClO_4$ and 0.05 M $ZnCl_2$ and were used as supporting electrolyte and zinc source, respectively. Each film was deposited at optimum growth parameters, determined from our previous studies [16–19], under the potential of −1.2 V, temperature of 100 °C and time of 3600 s. In order to check the reliability of the data obtained, ZnO thin films were grown on five Au decorated p-Si and five on the reference without Au NPs.

2.3. Characterization

The AuNPs and ZnO thin films were analyzed by X-ray Diffraction (Panalytical, Empyrean), Scanning Electron Microscopy (Zeiss, Sigma 300), diffuse reflectance (Shimadzu, UV3600), micro raman spectrometer (Witec, Alpha 300), Photoluminescence (Dongwoo Optron) and X-ray Photoelectron Spectroscopy (Specs, FlexMod). The current-voltage (I-V) characteristic of the hetero-junctions was tested by a Keithley 2400 source-meter unit.

3. Results and discussion

From the SEM images as shown inset in the Fig. 1, uniform distribution of the AuNPs across the p-Si substrate can be seen clearly where the dimensions of the AuNPs vary from 100 nm to 270 nm resulting in an average of 150 nm. Also from the figure, transmission spectrum of the Au thin films grown on the quartz substrate before and after being thermally processed can be seen. Similar transmission results were also obtained for the samples grown on p-Si substrates by diffuse reflectance measurements. Minimum transmission of 40% around near infrared region at 700 nm is obtained for the AuNPs processed at 600 °C on both p-Si and quartz substrates. The figure indicates the SPR frequency is around 700 nm for AuNPs for the size of 150 nm, while it is 520 nm for 12 nm AuNPs [14].

XRD measurements performed on the ZnO thin films grown on p-Si and AuNPs decorated p-Si substrates are shown in Fig. 2. Crystallographic planes (100), (002), (101) and (102) belonging to the ZnO hexagonal structure were observed. Also peak corresponding to Au (200) and (111) plane can be seen in the diffraction pattern of ZnO thin films grown on AuNPs/p-Si. Distinct variations are observed when both XRD spectrum compared. First of all, while the (002) plane is the

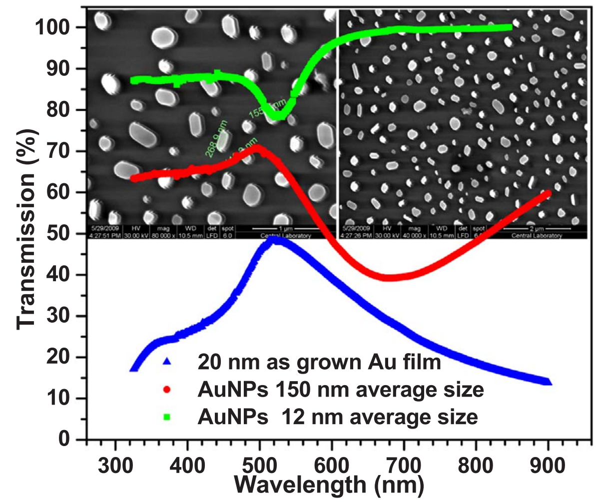

Fig. 1. Plot shows the transmission spectrum of Au thin films grown on p-Si substrate before and after thermal process. Insets are SEM images of the AuNPs formed on the p-Si.

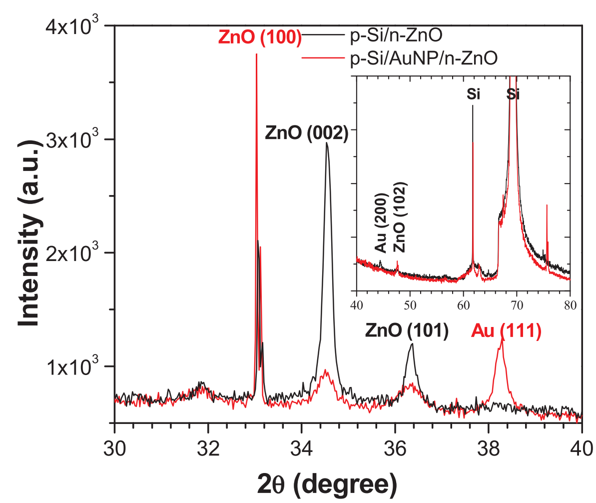

Fig. 2. The XRD spectrum of ZnO thin films grown on the p-Si and p-Si/AuNPs.

dominant plane for the ZnO thin film grown on p-Si as in our previous studies [16–19], it is observed that (100) plane is dominant growth orientation with using AuNPs decorated p-Si. The ratio of the intensities of the ZnO (100) and (002) planes ($I_{(100)}/I_{(002)}$), which are the two highest intensity peaks for both films, is 0.7 and 4.1 for the ZnO thin film grown on p-Si and AuNPs/p-Si, respectively. This confirms that there is a preferred growth orientation on the ZnO thin films grown on the AuNPs/p-Si substrate. Secondly, Full Width at Half Maximum (FWHM) of the dominant peaks changed which reflects the change in the sizes of the grains in ZnO thin films grown. The FWHM of the dominant (100) peak for ZnO thin film grown on AuNPs/p-Si substrate is 0.034° confirms a 252.4 nm grain size, while FWHM of dominant (002) peak for the ZnO thin film grown on p-Si substrate is 0.2° resulting from a 43.5 nm grain size. This crystallite size might be explained if the sides of the cuboid-like shapes of the AuNPs are electrochemically favorable for the ZnO thin film growths, determining the preferred growth direction. It might be speculated that the AuNPs plays a template like a role on the grown ZnO thin films which might be useful for many applications.

Fig. 3(a) and (b) show SEM images for the ZnO thin films grown on the Au decorated p-Si substrate, while Fig. 3(c) and (d) show the ZnO films grown on p-Si substrate. On the surfaces of the films is formed spherical shaped grains. What is clear from Fig. 3 is that larger grains formed for the thin film grown on the AuNPs/p-Si compared to that on