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Insight of dipole surface plasmon mediated optoelectronic property tuning of ZnO thin films using Au

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ABSTRACT

Surface plasmon mediated photoluminescence (PL) studies of ZnO, ZnO/Au, ZnO/Au/ZnO and Au/ZnO films have been investigated. An enhancement of UV and visible light emission has been observed in ZnO/Au and ZnO/Au/ZnO films, compared to that of ZnO thin films, while for Au/ZnO films quenching of PL intensity was observed. Excitation intensity (EI) dependent PL spectra have shown dominance of horizontal dipole surface plasmon mode for ZnO/Au/ZnO, ZnO/Au samples, which led enhanced greenish-yellow and orange emissions respectively. Moreover, confocal laser scanning microscope measurements and diffuse reflectance spectroscopy were conducted to investigate the mechanism behind the variations and involvement of Urbach tail. UV and visible region absorption were selectively enhanced by varying the Au and ZnO configuration and can be assigned to the interaction of the dipole surface plasmon resonance with localized trapping levels and phonon subsystem. The excellent photoluminescence performance has immense potential for ZnO thin film based optoelectronic devices.

1. Introduction

With the pioneering work by Okamoto et al., influence of metal coating over the optical properties of ZnO has attracted wide attention of scientific community [1,2]. Metals, most specifically noble metals have shown tremendous influence on the emission and absorption properties of ZnO [2–4]. Although, most of the reports have shown the effect of the metal coated over the top or bottom of ZnO, however there are still not many reports on the influence of metal layer inserted in-between ZnO films over the PL and absorption properties [5]. Metals in metal/semiconductor configuration are prone to various environmental contaminations like surface oxidation while adhesion and reduced transparency are major problems for semiconductor/metal configurations. Moreover, the tunability of emission and absorption properties for top coated configuration has limited room. A possible solution for the above mentioned issue is to insert the metal layer in between ZnO layers as the dipole surface plasmons can effectively improve the optoelectronic properties. In this article, we have focused on the PL and absorption properties of ZnO, Au on top of ZnO (Au/ZnO), Au layer in between ZnO layers (ZnO/Au/ZnO) and Au at bottom of ZnO (ZnO/Au) configurations, here defined as ZO, AZO, ZOAZO and ZOA respectively.

Surface plasmons (SPs) have attracted great attention due to their fundamental importance and potential applications in the enhancement of luminescence efficiency of light emitting materials and devices [1–6]. Localized surface plasmons (LSPs) arise when conduction electrons in metal nanoparticles (NPs) are resonant with the oscillating electromagnetic field of incident light. The resonance leads to field amplification both inside and in the near-field zone outside the metal NPs. The resonance frequency of LSPs rests with the shapes, sizes and orientation of metal NPs and the outside dielectric layers. Therefore, UV and visible light emission of ZnO can be enhanced or supressed selectively with the incorporation of semiconducting films with metal NPs. In this paper, we have studied the LSP mediated plasmon-exciton coupling in ZnO/Au/ZnO and ZnO/Au thin films. Interestingly, it was observed that when Au nanoparticles are completely immersed in ZnO, nearly three-fold enhancement of visible light emission from ZnO was observed, much higher than that from Au/ZnO configuration. Enhancement of emission is found to be dependent both on Au nanoparticle size and on ZnO layer thickness, which indicates that

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LSPs can effectively modulate visible light emission from ZnO.

Due to its wide band gap ZnO has absorption mainly in the UV region of the electromagnetic spectra, therefore its applications are limited to UV sensing and emissions [2,6,7]. Here we are reporting a systematic tuning of the absorption properties of ZnO with the change of the configuration of Au and ZnO layers. A significant increase in the visible region absorption of ZnO with Au layer inserted into ZnO layers has been observed. Additionally enhancement in the UV region absorption has been observed for ZOA configuration. The excitation intensity dependant PL has shown significant change in the type of oxygen defects mainly oxygen vacancies with film thickness and the effect of dipole surface plasmons [8,9]. Confocal microscopy studies have shown significant improvement in the uniformity of the emission sites for ZOAZO samples. Moreover, Urbach tail analysis for all the configuration was done, which has demonstrated the involvement of electron-impurity interactions towards the increased Urbach energy.

Metal coated ZnO thin films have shown variety of applications like enhanced UV and visible light detection, wave-guiding and second harmonic generation (SHG) [7,10–12]. The SHG depends promptly on the degree of crystallinity of the film, grain boundaries and their interfaces; and can be effectively improved using the surface plasmon resonance of metals as it will definitely enhance the local electric field near the metal NP and semiconductor interface [10,11]. The variation in the crystallinity, surface roughness, plasmon peak of Au, involvement of horizontal dipole surface plasmons and Urbach tail observed in various configuration of Au and ZnO can cause dramatic improvement in its optical properties for variety of applications [10,11,13]. The work presented has immense potential for ZnO thin film based optoelectronic and nonlinear optical devices.

2. Experimental procedures

The preparation process includes thin layer coating using solution method as reported in our previous works, in short a 2 M solution of zinc acetate and equi-molar ethanolamine in 2-methoxyethanol was spin coated at a rate of 3000 rpm for 30 s and later these spin coated samples were annealed at 250 °C for 5 min for ZnO thin film growth [6,7]. The deposition of 5 nm thick Au on these ZnO NRs was subsequently carried out by using dc sputtering system (Quorem (Q-150 RES)). The thickness of Au coating was measured using inbuilt crystal detectors. In this work the thicknesses of ZnO and Au layer were kept 100 and 5 nm respectively for systematic comparison [6,14]. The morphology of the products was observed by a field emission scanning electron microscope (FESEM), Zeiss Supra −55 equipped with energy dispersive spectra (EDS) (Oxford Instruments, X-MAX, 51-XMX1025). The PL spectrometer (Dongwoo Optron DM 500i) having an excitation source consisting of a continuous wave He-Cd laser (excitation wavelength, 325 nm, PMT detector) was used to measure the PL emission from these samples at room temperature. Confocal microscope images were obtained by using a Leica TCS SP5 confocal microscope equipped with PMT detector.

3. Results and discussion

Fig. 1(a–d) shows the top view FESEM images of ZO, ZOA, ZOAZO and AZO samples respectively (schematic is shown in Fig. 2). The thickness of ZnO in all four configurations was 100 nm, coated with 5 nm Au in every case. Moreover, the surface morphology of ZOAZO samples were rough as the heating of Au coated ZnO films covered with solution has promoted Au island formation thereby causing rougher surface. The surface morphology of AZO film became a compact and smooth structure.

XRD plots for the samples are plotted in Fig. 3. A dominating (002) peak along with (100), (101), (110) and (112) was seen for all samples [6]. Moreover the ratio of the intensity of (002) peak versus (100) peak was higher for ZOAZO and ZOA samples in comparison with ZO samples, while it was low for AZO samples indicating covering of ZnO film with Au [15]. Now, it must be noted that the 2θ value for Au (111) peak decreased for ZOA samples (by about 0.15°) and ZOAZO (by about 0.11°) samples, which can be assigned to the growth of nanoparticle sized Au by Ostwald ripening [16]. Moreover the sharpening of the peak of Au (111) centered at 38.4° indicated decreased surface tension of Au particles [16]. The broadening of (002) peak for ZOA and ZOAZO samples can be simply assigned to the increased crystallite size and induced strain due to annealing.

Fig. 4 shows the emission spectra of ZO, AZO, ZOA and ZOAZO samples. As grown ZO samples have shown a strong emission in the UV region (peak cantered at 390 nm) and a feeble yellowish-green emission. The UV emission peak is actually near band edge emission (NBE) due to recombination of excitons. While the visible emission can be assigned to various defect related emissions (DLE), mainly owing to oxygen vacancies and interstitials [6].

Interestingly with Au coating drastic change in the NBE and DLE peak positions and intensity has been observed. It can be seen in Fig. 3 that both NBE and DLE are enhanced for ZOA and ZOAZO samples, while significant quenching for AZO samples was observed. The enhancement factor for NBE and DLE were 1.2 and 2.2 for ZOA samples and 2.8 and 1.7 for ZOAZO samples respectively. Interestingly, the visible emission peak for ZOA samples shows significant defect related emission with peak centered at 582 nm for ZOA samples while for ZOAZO samples at 530 nm. Although for AZO samples the DLE was suppressed in comparison with ZnO samples, with the DLE peak centered at 594 nm. The emission enhancement can be attributed to the coupling of the radiation field with surface plasmons in Au [2]. Now, for ZOAZO smaples, the radiation field originates from spontaneous recombination in ZnO, which further induces oscillating dipoles inside the Au (sandwiched between ZnO layers) instead of escaping into free space. When the frequency of the dipoles is approximately the same as the radiation field, a resonance condition is reached, which is known as dipole surface plasmons (DSPs) [17]. The enhancement in the emission intensity can be attributed to the increased scattering efficiency of Au nanoparticles due to DSPs, as the Au layer is sandwiched between two ZnO layers [9,17].

As mentioned earlier, for ZOA and ZOAZO samples the intensity of both the ZnO (002) and Au (111) peaks increased due to the annealing of the top layers at 250 °C. This finding can be understood based on the fact that the thermal energy during annealing may enable atoms to diffuse and stack. As a result, a more perfect crystal structure was obtained as has been discussed earlier, which thereby cause formation of two dipoles one along the Au plane i.e. horizontal resonance and the other one perpendicular to the Au plane i.e. vertical resonance [17,18]. The horizontal resonance wavelengths are sensitive to the ZnO thickness and for ZOA samples (100 nm thick ZnO layer over Au layer) enhances visible emission primarily centered at 582 nm, while in the case of ZOAZO samples vertical resonance play dominating role thereby leading to enhanced green emission [17,18].

In addition to this, heat generation at nanoparticle site, with optical illumination play a significant role in the Plasmon resonance regime of Au embedded in ZnO films. The maximum increase in the temperature as a function of light intensity, I_0 may be written as [19]:

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