Au/nc-Si:H core–shell nanostructures prepared by hot wire assisted plasma enhanced chemical vapor deposition technique

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ARTICLE INFO

Article history:
Received 10 October 2011
Accepted in revised form 25 April 2012
Available online xxxx

Keywords:
Au/nc-Si:H core shell nanostructures
Silicon suboxide
HW-PECVD

ABSTRACT

In this study, Au film was embedded in Si:H film on quartz substrate with and without an SiO$_x$ layer by using the hot wire assisted plasma enhanced chemical vapor deposition (HW-PECVD) technique. The as-prepared Au/Si:H films were post-thermally annealed at 800 °C in nitrogen ambient in order to initiate the growth of Au NPs. The annealed Au/a-Si:H film deposited on quartz substrate without an SiO$_x$ layer showed the formation of well-distributed and spherical Au NPs. Formations of Au/nc-Si:H core shell nanostructures were observed on annealed film deposited on quartz substrate with an SiO$_x$ layer. XRD and micro-Raman scattering spectra revealed that the degree of crystallinity of nc-Si:H was dependent on the annealing temperature and interaction between a-Si:H film and SiO$_x$ layer. Optical spectra showed that the Au NPs on annealed films deposited on quartz substrate without an SiO$_x$ layer exhibited prominent SPR peak while annealed Au/nc-Si:H core shell nanostructures showed increased reflectance of light in the visible region.

1. Introduction

Hydrogenated nanocrystalline silicon (nc-Si:H) has attracted a significant amount of attention over the past decades due to its intriguing characteristics such as low optical absorption, high carrier mobility and conductivity as well as better stability against light induced degradation [1-5]. It has been utilized in a broad range of applications which include light emitting diodes, thin film transistors, solar cells and other optoelectronic devices [3,5,6]. With this said, gold nanoparticles (Au NPs) have also been extensively studied in recent years [7,8]. Unlike bulk Au, Au NPs are well known to exhibit the localized surface plasmon resonance (LSPR) phenomenon which can produce a strong scattering of light at particular visible wavelengths [7,9,10]. The possibility of tuning the LSPR wavelength, which is dependent on the size, shape, inter-particle distance and surrounding medium of NPs, has painted them as potential candidates for efficient light harvesting in plasmonic solar cells [11-14]. However, Au has a tendency to spontaneously agglomerate, resulting in the loss of interesting properties specific to its nanoscale size [15,16]. In this case, silicon suboxide (SiO$_x$) is the material used to prevent the aggregation of Au NPs, as reported in previous studies [17-19].

Undoubtedly, nanocomposite materials having interesting properties which are possessed by both Au NPs and nc-Si:H film. These properties are crucial in important applications such as nanoparticle-based optoelectronic and photovoltaic devices. This has been demonstrated by S. Mohapatra et al. [20] where Au–Si core–shell NPs with tunable LSPR were synthesized. By varying the volume fraction of Si nanoshells, the LSPR wavelength of Au NPs can easily be tuned. Nevertheless, the preparation of Au core surrounded by nc-Si:H shells has always been regarded as a challenging task due to the metal induced crystallization (MIC) of a-Si:H film embedded with Au. In this work, Si:H and Au films were first simultaneously prepared on the quartz substrate with and without an SiO$_x$ layer using the hot wire assisted plasma enhanced chemical vapor deposition (HW-PECVD) technique. The as-prepared Au/Si:H films were then thermally annealed at 800 °C for 1 hour. As is evident from our previous study, annealing at 800 °C for 1 hour is the optimal annealing parameter for the growth of Au NPs [18]. Higher annealing temperature can initiate MIC, leading to the formation of nc-Si:H film. The aim of this work was to study the role of the SiO$_x$ layer and annealing effect on the synthesis of Au/nc-Si:H core–shell nanostructures.

2. Experimental details

SiO$_x$ layers were first deposited onto the plain quartz substrates using a homebuilt PECVD system, as described elsewhere [18]. The precursor gases used were SiH$_4$ and N$_2$O gases with flow rate of 2 and 60 sccm respectively. Parameters such as deposition time, process pressure, substrate temperature and RF power were kept at 60 minutes, 1.0 mbar, 300 °C and 100 W respectively throughout the entire process. After SiO$_x$ deposition, the chamber was evacuated and opened. Following this, a piece of plain quartz substrate was placed onto the substrate holder in the deposition chamber together with the as-deposited quartz substrate with SiO$_x$ layer. Next, a piece of...
of gold wire with diameter and length of 0.5 and 4.0 mm respectively, was hung onto a helical tungsten filament, which was used as the heating element in this deposition system. The schematic diagram of the system can be obtained from Ref. [21]. The Au/Si:H films were then prepared simultaneously by evaporating the Au wire and discharging SiH₄ and H₂ gases using a HW-PECVD system which is similar to the technique found in Ref. [22]. The flow rates of SiH₄ and H₂ gases were kept at 2 and 80 sccm respectively. The deposition time, process pressure, substrate temperature and RF power were set at 30 minutes, 0.8 mbar, 200 °C and 100 W respectively. The filament temperature was fixed at 1400 °C and activated for 3 s for evaporation of Au. This process was only initiated after 15 minutes of deposition of Si:H film. A shutter assembled below the hot wire was used to control the evaporation time of Au. The as-prepared Au/Si:H films were then post-annealed at 800 °C for 1 hour in nitrogen ambient. The surface morphology of the samples was studied using a field emission scanning electron microscope (FESEM) (model FEI Quanta 200). The crystallinities of the samples were investigated using a Siemens D 5000 X-ray diffractometer (XRD) with Cu-Kα radiation, (λα = 1.54056 Å) and a micro-Raman spectrometer (InVia Renishaw). The optical absorption and reflectance spectra of the samples were measured using a JASCO V-570 ultra-violet/visible/near-infrared (UV–VIS-NIR) double beam spectrophotometer within a scanning range of 250 to 1200 nm.

3. Results and discussion

FESEM images of the as-prepared and annealed Au/Si:H film on quartz substrate without an SiOₓ layer are shown in Fig. 1(a) and (b) respectively. Au islands can be clearly observed on the as-prepared samples. The annealing process tends to decrease the surface energy of the Au islands resulting in the formation of non-uniform size but spherical shaped Au NPs. Quartz substrate is known as highly crystalline SiO₂. Thus, agglomeration of Au NPs can be barely observed despite the absence of the SiOₓ layer. The results suggested that the nucleation sites for the growth of Au NPs were abundant on plain quartz substrate. It is likely that Au atoms or particles smaller than a certain critical size preferentially coalesce at these sites via thermal diffusion when being annealed at a high temperature. Fig. 1(c) and (d) show an FESEM image of the as-prepared and annealed samples deposited on quartz substrate with SiOₓ layer. Some of the Au NPs on the as-prepared samples were seen to be already surrounded by Si shell. These indefinite core–shell nanostructures with Au NPs as their core became more significant after the annealing process. Clusters of core–shell nanostructures were evenly distributed on the surface of film. In general, the influence of substrate on the growth process of plasma-deposited semiconductor film was not an unexpected effect. In this work, during the deposition of a-Si:H film, SiH₄ plasma exposure resulted in the chemical reduction of the SiOₓ layer [23]. The oxide layer was reduced together with the inter-diffusion between constituent atoms of SiOₓ layer and a-Si:H, resulting in an increase in the number of Si atoms in the mixed phase of a-Si:H and SiOₓ. It should be noted that such a reaction is not significant between quartz substrate and a-Si:H due to the dependence of this effect on the surface properties of the substrate [24]. Further along in the growth process, molten Au–Si liquid droplets were easily formed since the eutectic temperature of the Au–Si system was 363 °C which is much lower than the annealing temperature of 800 °C [20]. These nanodroplets enhanced the diffusion process for metal induced crystallization (MIC) and reduced the activation barrier for favorable thermodynamic transition from amorphous Si to the crystalline Si phase [25]. During the high temperature annealing process, more Si atoms from the mixture of a-Si:H and SiOₓ were taken by the molten Au–Si liquid droplets. When the sample was left to cool down naturally, Si atoms diffused out to the surface of Au–Si nanodroplets forming an nc-Si:H layer around it, and thus leaving the Au NP intact at the centre. As a result, formation of the Au/nc-Si:H core shell nanostructures could be observed. The SiOₓ

![Fig. 1. FESEM image of as-prepared (a) and annealed (b) Au/a-Si:H film deposited on quartz substrate without SiOₓ layer and as-prepared (c) and annealed (d) Au/nc-Si:H film deposited on quartz substrate with SiOₓ layer.](image-url)
layer played a critical role since its inter-diffusion with a-Si:H gave rise to an increase in the number of Si atoms which was then taken by molten Au–Si droplets. The reduced compactness of the SiO_x layer also facilitated the formation of molten Au–Si liquid nanodroplets. This undoubtedly enhanced the probability of forming Au core surrounded by nc-Si:H shell nanostructures. This can be shown by observing the nc-Si:H phase in the film on quartz substrate with SiO_x layer, even in the as-prepared film.

Fig. 2(a) and (b) show the X-ray diffraction (XRD) pattern of the as-prepared and annealed Au/a-Si:H film deposited on quartz substrate without and with a SiO_x layer respectively. Au diffraction peak with different crystallographic plane of (111), (200), (220), (311) and (222) can be clearly identified. These corresponded to the 2θ angles of 38.2°, 44.4°, 64.6°, 77.7° and 81.2° respectively. It is evident from Fig. 2(b) that the nc-Si:H phase was only present in the annealed film deposited on quartz substrate with SiO_x layer. This is confirmed by the presence of diffraction peaks located at 2θ angles of 28.4°, 47.3° and 56.1° which corresponded to the (111), (200) and (311) crystallographic orientation planes of c-Si respectively. The crystalline grain sizes (D) of Au and Si in the films with and without SiO_x layer were determined from the full width at half maximum (FWHM) of diffraction peaks by using Scherrer's formula [26]. From the figure, it is evident that the size of Au crystallites increased after the annealing process. Au crystallites in annealed films without SiO_x layer were found to be bigger than the Au in core shell nanostructures (D = 38 nm). The estimated crystallite size of Si nanocrystals in orientation of (111), (200) and (311) was 34.0, 44.1 and 21.3 nm respectively.

The Raman spectra of the as-prepared and annealed Au/a-Si:H films deposited on quartz substrate with SiO_x layers are shown in Fig. 3(a) and (b) respectively. It was established that Raman peaks at 520 and 480 cm\(^{-1}\) corresponding to the transverse-optic (TO) mode of crystalline and amorphous Si respectively. However, Au/a-Si:H film deposited on quartz substrate without SiO_x layer (not shown here) showed no observable Si Raman peak even for the annealed film, possibly due to the high photoluminescence signal of this film in this particular region. Nevertheless, asymmetric sharp Raman peaks at 513 and 516 cm\(^{-1}\) were observed in the spectra of the as-prepared and annealed films with SiO_x layer respectively. The downshift of the Raman peaks of TO mode of c-Si to lower wavenumber from 520 cm\(^{-1}\) suggested that these films consist of Si nanocrystallites embedded within the amorphous matrix [2,21,27]. The size of Si nanocrystallites, D_R can be estimated from the downshift in this Raman peak using the following equation [2]:

\[
D_R = 2\pi \sqrt{B \Delta w \over \Delta \omega}
\]

where B is 2.24 cm\(^{-1}\) nm\(^2\) for silicon and \(\Delta \omega\) is the Raman shift of crystalline peak from single crystalline peak located at 520 cm\(^{-1}\). \(D_R\) values determined from this equation for as-prepared and annealed samples were around 3.3 and 5.5 nm respectively, showing that the size of Si nanocrystallites increases following the annealing process. It is evident from the literature that grains smaller than around 5 nm are not sensitive to the XRD spectra [2]. This fact
accounts for the absence of the diffraction peak of c-Si in XRD pattern of the as-prepared sample. The difference in detection sensitivity of the characterization technique has resulted in the difference in measured crystallite size using Raman and XRD spectra. However, the variation of $D_k$ is consistent with the crystallite sizes estimated using XRD spectra. It is important to note that results obtained from both techniques showed the same trend. The Raman spectrum for as-prepared sample was de-convoluted into three component peaks using the Gaussian function fitting. The crystalline volume fraction, $X_C$, for the nc-Si phase in the film, was calculated using the three peaks method [3]:

$$ X_C = \frac{I_c}{I_{gb} + I_a + I_c} \times 100 $$(2)

where the $I_a$, $I_{gb}$, and $I_c$ represent integrated intensities of amorphous, grain boundaries, and crystalline phase at around 480, 500 and 520 cm$^{-1}$ respectively. The crystalline Si volume fraction of the Si:H phase in the film deposited on the SiO$_x$ layer was found to increase from 32.5% to 62.0% following the annealing process.

Fig. 4 shows the absorption and reflectance spectra of as-prepared and annealed Au/Si:H film deposited on quartz substrate with and without SiO$_x$ layer. The Au/nc-Si:H film deposited on the quartz substrate with SiO$_x$ layer showed higher absorption when compared to that of the film deposited on plain quartz substrate. The as-prepared Au/a-Si:H film deposited on plain quartz substrate exhibited a broad SPR peak at around 550 nm and this peak increased in sharpness and blue-shift to 480 nm after being annealed. Furthermore, a broader SPR peak located at around 500 nm was observed in the absorption spectra of Au/nc-Si:H core–shell nanostructures. This absorption peak became slightly narrower and red-shift to 530 nm following the annealing process. It has been established by Mie theory that SPR peak positioned in this region is attributed to the Au nanospheres [28]. The shift in the SPR peak position is usually related to the change in shape of Au NPs [7,11]. For instance, as discussed earlier, the core–shell nanostructures and spherical Au NPs were clearly observed in the Au/Si:H film deposited on the quartz substrate with and without SiO$_x$ layer respectively. Furthermore, the intensity and sharpness of SPR peak in both samples were further increased and narrowed following the annealing process as a result of the increase in size of Au NPs. This phenomenon was found to be consistent with results reported in similar works [7,29,30]. From the reflectance spectra, the as-prepared and annealed Au/nc-Si:H core–shell nanostructures exhibited lower and higher reflectance in the visible region when compared to the as-prepared and annealed film deposited on plain quartz substrate. Furthermore, the presence of a small but observable peak in the UV region could be observed, indicating the presence of Si nanocrystallites in the film [31] as confirmed by the Raman results.

4. Conclusion

The results showed that Au/nc-Si:H core–shell nanostructures were successfully synthesized through simultaneous evaporation of Au and discharge of SiH$_4$ and H$_2$ gases using the hot wire assisted PECVD technique. Well distributed and spherical Au NPs embedded within a-Si:H film were grown on quartz substrate without an SiO$_x$ layer. Annealing temperature and the interaction between SiO$_x$ and a-Si:H films were prerequisites for the growth of Au/nc-Si:H core shell nanostructures and enhanced the degree of crystallinity of nc-Si:H film. A prominent LSPR peak induced by Au NPs was found on the Au/a-Si:H film deposited on quartz substrate without SiO$_x$ layer. The LSPR wavelength and intensity were in line with results reported in similar works [7,29,30]. From the reflectance spectra, the as-prepared and annealed Au/nc-Si:H core–shell nanostructures exhibited lower and higher reflectance in the visible region when compared to the as-prepared and annealed film deposited on plain quartz substrate. Furthermore, the presence of a small but observable peak in the UV region could be observed, indicating the presence of Si nanocrystallites in the film [31] as confirmed by the Raman results.

Acknowledgments

This work was supported by a University Malaya Research Grant (RG069/09AFR), Ministry of Higher Education (FP045/2010B), and Postgraduate Research Fund (PV007/2011B).
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