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Fabrication of substrate supported bimetallic nanoparticles and their optical characterization through reflection spectra

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ABSTRACT

An approach for the fabrication of bimetallic (Au–Ag) nanoparticle is investigated and its optical response in terms of refection spectra is obtained. A bimetallic film is deposited on a c-Si substrate followed by thermal dewetting at 800 °C for 15 min. Randomly dispersed bimetallic nanoparticles are formed on the substrate. The sequence of deposition of the metallic film is reversed and reflection spectra for all the samples including the bare c-Si is obtained. It is seen that the reflection of the bimetallic nanoparticle dispersed c-Si substrate is less than the bare c-Si for almost all the wavelengths ranging from 300 to 1100 nm due to the localized surface plasmon resonance of the bimetallic nanoparticles.

1. Introduction

Metallic nanoparticles are emerging as key components in a wide range of applications such as plasmonics [1,2], sensors [3], DNA detection, Surface enhanced fluorescence [4], magnetic memories [5], high density data storage [6], improving efficiency of solar cells [7], catalysis for growth of nanowire [8], label-free visualization of living cells [9] etc. In solar cells, the LSPR (localized surface plasmon resonance) of the metallic nanoparticles enables it to trap the light incident on it, thus reducing the reflection and in turn increasing the efficiency of the solar cells [10–14]. Thermal dewetting is the easiest and least complicated method to convert a deposited metallic thin film into metallic nanoparticles. The metallic film deposited through DC sputter coating is metastable in nature and upon receiving a thermal impetus, the atoms at the surface migrate to form individual islands which ultimately forms the metallic nanoparticles [15]. The complete process is driven by minimization of the surface energy of the deposited film [16]. Literature is available on the fabrication and optical characterization of different metallic nanoparticles however only limited literature is available on bimetallic nanodots and their optical response.

2. Experimental methodology

Crystalline silicon (c-Si) wafer of p-type with 380 μm thickness was used as a substrate material. Samples were then cleaned in an ultrasonic probe-sonicator at 70 W power for 10 cycles of 15 s duration with 5 s idle time between each samples. The cleaning through probe sonication was carried out in acetone. Once the samples were cleaned, they were taken out and air dried. Thereafter the samples were transferred to the chamber of DC sputter coater for deposition of the metallic films. The deposition was carried out in a chamber pressure of 2 mbar. Gold and Silver deposition was carried out at sputter currents of

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25 mA and 50 mA respectively. Initially 5 nm of Au was deposited and it was followed by 5 nm of Ag (hereafter referred as Trial Sample) and thermal dewetting was carried out to observe the formation of the nanoparticles formed. Once it was confirmed that through thermal dewetting a bimetallic film can be transformed into a randomly distributed bimetallic nanoparticle array, two sets of samples were fabricated (whose reflectance spectra were studied at later stage): 10 nm of Ag was deposited followed 10 nm of Au (hereafter referred to as Sample A) and 10 nm of Au was deposited followed by 10 nm of Ag (hereafter referred to as Sample B).

After the deposition, all the samples were put into furnace for thermal dewetting. A microprocessor-based-temperature-controlled-furnace was used for the thermal dewetting. The dewetting of Trial Sample was carried out at 750 °C since the films having lower thickness could dewet at lower temperature. The driving force for dewetting increases with the reduced film thickness [16]. The dewetting of Sample A and Sample B (which are of 20 nm overall thickness) was carried out at 800 °C for 15 min. To achieve this, first the temperature of the furnace was ramped up to the desired temperature. Once the temperature was reached, the furnace door was opened and the coated sample was put inside the furnace. A drop of few degrees in temperature took place in the time interval in which the sample was put inside the furnace, so the timer was started only after the desired temperature was attained once again. The samples were left inside the furnace for the desired time i.e. 15 min for these experiments. Once the soaking time was completed the furnace was switched off and the furnace door was immediately opened to take out the crucible in which the samples were kept. The samples were then air cooled (which takes 30–50 s) and then they were transferred for optical characterization.

Perkin Elmer Lambda 1050 UV/VIS/NIR spectrophotometer was used for optical characterization of the randomly dispersed bimetallic nanoparticles for wavelength ranging from 300 to 1100 nm.

3. Results and discussion

3.1. Fabrication of randomly dispersed bimetallic nanoparticles

The bimetallic films get converted into randomly dispersed nanoparticles after the thermal dewetting. It has been proved previously [17] that a bimetallic film of Au and Ag gets converted into a nanoparticle in which the Au and Ag is homogeneously distributed. So although initially the deposited film has clear delineation between the Au and the Ag layer, once the thermal dewetting is carried out, it gets converted into a homogeneous alloy nanoparticle as shown in Fig. 1(a).

The AFM and SEM images of the substrate supported nanoparticles is shown in Fig. 1. From the AFM and the SEM images it can be observed that the continuously deposited film has broken into randomly distributed nanoparticle after the thermal dewetting. The particle shape is predominantly spherical but some deviations are also observed as can be seen from Fig. 1(c) where some particles are elongated rather than being spherical. It can be seen that the substrate is not damaged during the thermal dewetting and only the deposited metallic film is affected by the process. It is also observed from Fig. 1 that the contact angle is more than 90°, which is good for forward scattering of light into the substrate.

The dewetted samples and their SEM micrographs are shown in Fig. 2(a–e). As can be seen from Fig. 2(a), (b) and (c); after thermal dewetting the deposited bimetallic film transforms into randomly distributed nanoparticles. In the case of Trial Sample the particles are almost perfectly circular, as observed from the top, which implies that they are spherical nanoparticles.

The size of the nanoparticle increases with the increase in the total thickness of the deposited bimetallic film as can be observed from distribution of particle size shown in Fig. 2(d), (e) and (f). The average particle size for Trial Sample is 90 nm, whereas for Sample A and Sample B the average size is 275 nm and 310 nm respectively.

3.2. Reflection spectra and ultimate efficiency calculation

The reflection spectra for bare sample, Sample A and Sample B, for the wavelength range of 300–1100 nm is shown in Fig. 3. A maxima in the reflectance spectra can be seen at lower wavelengths ~375 nm. This is attributed to direct electronic transition in c-Si. With introduction of metal nanoparticles on the top surface of c-Si the spectral position of the reflectance maxima does not change. The magnitude of this reflectance maxima for Sample A and Sample B is lesser than that of bare c-Si due to the interband transitions and the reduction in the refractive index mismatch [17]. This is followed by small dip in the reflectance spectra at ~400 nm. The dip is attributed to the quadrapolar resonance of the bimetallic nanoparticle.

After the dip at ~400 nm the reflectance spectra steadily increases to another maxima. This maxima is located roughly in the centre of the considered spectrum and the value of the reflectance peak is also higher than the maxima in the reflectance curve obtained at lower wavelengths. The maxima for Sample B (having Ag on top) is in fact higher than that of the bare c-Si. And.

After this maxima, the reflectance again falls down till ~1000 nm. This region is important because in case of uni-metallic nanoparticle (of Au or Ag) the reflectance curve for the nanoparticle generated from higher film thickness goes above the reflectance of the bare c-Si, thus increasing the overall reflectance. But in case of bimetallic nanoparticles on c-Si substrate the reflectance curve moves down from the bare c-Si and thus enhances the performance by reducing the overall reflectance.

It is observed that the reflectance increases slightly after ~1000 nm, this could be attributed to the increase in absorption depth at higher wavelengths due to which back reflection takes place which increases the reflectance. But the reflectance for