Surfactant Growth and Optical Studies of Plasmonic Silver Nano-Disks

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Infrared spectroscopy is used as an optical probe to spectrally characterize and tailor the lateral growth of silver nanostructures on silicon reconstructed surfaces. The silver nanostructures are prepared in ultra high vacuum environment by depositing silver onto a surfactant pre-covered silicon substrate, followed by an annealing step. Transmittance spectrum in mid-infrared region of the as-deposited film shows a tail arising from the Mie resonance of individual nano-particles whose resonant features located in visible region. After annealing, the aggregation of particles forms an atomically flat ensemble of nano-disks resulting in a significant shift of plasmonic resonance to mid-infrared. Surprisingly, this resonance position can be tuned over the entire mid-infrared range by varying the diameter of the disks. The finite different time domain simulation is performed to give a better insight into the behavior of this resonant class and proofs the existence for the dipolar resonance thereby confirms the antenna resonance of the nano-disks. [DOI: 10.1380/ejssnt.2012.239]

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I. INTRODUCTION

Metal nanostructures working at the optical frequencies are of great interests since they operate as plasmonic nano-antennas that can manipulate light on the nanoscale, providing possible applications in future electronics and bio-technology [1–5]. Amongst the plasmonic materials, silver offers the lowest plasmon loss [4]. A silver film can support plasmon propagation length of about 10 μm [4]. The plasmon loss is defined by the energy loss function, which depends on the imaginary part of the dielectric function of the metal used and the surrounding media 1/Im(ε(ω)). For a certain material, the resonance position of a plasmonic structure depends on the size and the lateral shape of the object. To make the plasmonic enhancement effective, there is a demand to tune the plasmon energy to match with the specific frequency range [3]. Unlike the case of metal particles whose resonant frequency is theoretically limited within ωp/√2 and ωp/√3 (ωp is plasma frequency of bulk metal), the metal nano-rods offer much stronger tunability [6–8]. It is worthwhile to examine whether the quasi two-dimensional films (nano-disks) can support such a dipole resonance with a comparable tunability.

In this report, we present our novel method to grow the flat silver disks that show the plasmonic resonance in the infrared spectral region. An In(111)-7 RT substrate was cleaned in UHV with a standard procedure described in reference [9]. About 1/3 monolayer (ML) of In was then evaporated onto the Si(111)-7 × 7 RT substrate (hereafter referred as: Si-7 × 7) following by annealed at 500 °C for 30 seconds to form Si(111)-7 × 3 ML (hereafter referred as: In√3) reconstructed surface. Silver nano-disks were prepared by physical deposition of Ag onto In√3 RT substrate, then annealed at about 70–80 °C for 3 minutes. Thickness of In (and Ag) coverage was calibrated by RHEED monitoring the surface transition from Si-7 × 7 structure to (√3 × √3) reconstruction [10]. One ML of In (and Ag) corresponds to the atom density of the Si(111) plane (7.84 × 10¹⁴ atom/cm²). The FTIR

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spectroscopic measurements were performed in the transmission geometry (normal incident angle) with resolution of 4 cm$^{-1}$.

III. RESULTS AND DISCUSSION

Growing the atomically flat disk-like structure on Si-7×7 substrates is still quite challenging [11, 12]. The previous studies showed that the obtained structures are usually not well-ordered in shape since the Si-7×7 substrate is chemically active with dangling bonds on the surface [13]. Therefore, chemical property of the Si template plays a key role in the formation of the Ag nanostructures. Additionally, the IR spectral study on such surface provides information about the AC conductivity of the surface [14] which also reflects the chemical characteristics of the surface. With an insulating substrate, the supported Ag structures are in non-interacting regime and electrically isolated. We attempt to use In$\sqrt{3}$ as substrate since it is known to be a two-dimensional insulating phase and offers well-defined surface reconstruction over entire surface area [15].

Figure 1 presents two experimental results that are used to examine the In$\sqrt{3}$ surface property. Figure 1(a) shows the electron diffraction by RHEED on Si-7×7 and In$\sqrt{3}$ surfaces, electron beam energy was 20 keV. The RHEED pictures show sharp diffraction spots for the obtained In$\sqrt{3}$ phases, suggesting that In$\sqrt{3}$ is a unique phase and has large domain size. As reported previously by J. M. Nicholls et al. [15], In$\sqrt{3}$ surface is an insulating phase having an indirect band-gap of about 1.5 eV. We give here another possibility to detect this surface characteristic by using FTIR spectroscopy. Figure 1(b) presents the relative transmittance spectra of Si-7×7 and In$\sqrt{3}$ measured at RT. It is obvious that the In$\sqrt{3}$ surface has higher transmittance than Si-7×7 in the range starting from 4500 cm$^{-1}$ to far infrared (well-below 1000 cm$^{-1}$). The anti-reflection feature of In$\sqrt{3}$ compared to Si-7×7 reflects that this phase has smaller conductivity than Si-7×7. In other words, density of states of In$\sqrt{3}$ is smaller than that of Si-7×7 surface, making it possible for 2-D long range diffusion of Ag adatoms on its surface with reduced adatom-substrate interaction to form large Ag disks by 2-D Ostwald ripening.

Figure 2 presents the photon-induced excitation of plasmonic resonance of the prepared silver nanostructures. The blue line (100% transmittance) shows the normalized spectrum from the same initial In$\sqrt{3}$ surface right before the deposition of Ag. The black curve shows the transmittance of the as-deposited silver film with thickness of 1.6 ML normalized to the reference spectrum taken from the In$\sqrt{3}$ surface. The decrease of the transmittance at higher energy (higher frequency) appears as a tail of a resonance in the visible. One can expect that this tail comes from the conventional Mie resonance of small particles with an average diameter below 10 nm, lying on top of the inert In$\sqrt{3}$ template (see AFM image in Fig. 2(b)). Upon thermal annealing at about 70-80°C, huge silver nano-disks emerge on the substrate with average diameter of about 500 nm, and with an approximately uniform thickness of 15 nm. The typical density of nano-disks in the annealed sample (2 ML coverage) is estimated of about $9.7 \times 10^{13}$ cm$^{-2}$ and the typical morphology of the disks is shown on the AFM image (Fig. 2(c)). Interestingly, the corresponding FTIR spectrum of Ag disks exhibits well-defined single resonance in mid-infrared. In addition, we observe larger nano-disks when the annealing time increased. Correspondingly, a larger red-shift of the resonance frequency is observed (not shown). The shift of the resonance position from visible to mid-IR corresponds to different disk diameters, showing an evidence of a dipolar resonance. This type of results also found on previous study for the case of the fundamental excitation standing wave plasmons in metal nano-rods and atomic wires [3, 16].
FIG. 2: (a) The FTIR spectra of as-deposited Ag film and Ag disks on In\(\sqrt{3}\) surface, taken at room temperature. (b) the corresponding atomic force microscope (AFM) pictures of as deposited sample and the annealed sample (c).

FIG. 3: (a) Electromagnetic simulation of the single disks with various diameters, ranging from 200 nm to 800 nm. (b) Simulated electric field distribution at the excitation wavelength matching with resonance frequency of the object (2500 cm\(^{-1}\)). Color bar depicts the amplitude of electric field in the structure.

To further elucidate the antenna resonance of the nanodisks, we performed the electro-magnetic simulation (finite different time domain - FDTD, rigorous coupled wave analysis - RCWA) to simulate the measured spectra [17]. Thickness of the disks is kept as constant (15 nm) meanwhile the disk diameter is varied from 200 nm to 800 nm. The simulation for pure Si substrate is also done to obtain the reference spectrum. The dielectric functions for describing the optical property of the materials used in this study are taken from literature [18]. Figure 3(a) shows the simulation results for various disk diameters. The relative transmittance displays a red shift to lower energy (lower frequency) when the disk diameter is increased, which is in good agreement with the experimental finding. This low energy shift is directly related to the dipolar excitation in the disk due to the formation of plasmon standing waves. Further, the FDTD simulation (Fig. 3(b)) displays the electrical field distribution over the disk under the illumination of its resonant wavelength (\(\lambda_{exc} = 4\) \(\mu\)m for this case). It shows that electric field is enhanced at the ridges of hexagon depending on the polarization of impinging radiation. The enhancement factor at the corners

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/)
is about 16 times higher than that of the free space.

IV. CONCLUSIONS

In summary, we have presented a novel method to grow the flat 2-D nano-disk on a chemically modified silicon template. The insulating InP template, whose chemical reactivity (surface metallicity) has been characterized by the FTIR, could make a 2-D diffusion for silver adatoms thereby forming the nano-disks. Although transmittance spectrum of the small Ag particles displays a tail in the IR region, the formation of the disks demonstrated a clear resonance in mid-IR region. The diameter-dependent resonance is then assigned to the antenna resonance and found to be in good agreement with electro-magnetic simulation. The electric field enhancement at the vicinities of the disks makes them possible to be utilized for future plasmonic sensors or novel solar cell working in the infrared region. Our work provides new insight into the plasmonic resonator using low-dimensional metallic nanostructures.

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