Characterization of plasmonic nanostructures by analytical TEM

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Abstract. A combination of electron microscopy and spectroscopy techniques has been applied to investigate the properties of metallic nanoparticles for applications as plasmonic materials. Gold nanoparticles have been deposited on Si and SiC semiconductor substrates to evaluate their structural and chemical properties at atomic scale resolution. High resolution imaging has been used to study the atomic structure of the nanoparticles and interfaces. The chemistry of the nanostructures has been analysed using energy-filtered TEM, electron energy-loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDS).

1. Introduction

Metallic nanoparticles (NPs) exhibit surface plasmon resonance (SPR) that occurs at a metal/dielectric interface and provides the opportunity to confine light to very small dimensions. Plasmonic NPs are of considerable interest due to plasmon tunability and potential applications as biosensors, photonic, optoelectronic and photovoltaic devices [1]. These applications rely on the fabrication of Au NPs on technologically important substrates and on the possibility to control the SPR properties. A number of experimental and theoretical investigations of the optical and structural properties of Au NPs have been carried out [2-7]. Au NPs have been found to exhibit SPR and it has been found that their optical properties are related to the size and shape of the Au NPs-based nanosystems. In the case of Au NPs on a silicon substrate, it has been shown that interface characteristics such as interfacial SiO₂ and gold silicide formation also affect SPR properties. However, the correlation between the SPR properties and interfaces in Au nanosystems is not clearly understood.

Au NPs have been deposited by Ar sputtering onto Si (111) and SiC (0001) single crystal substrates. The deposition time and the substrate temperature were varied to synthesize NPs of different sizes (10-60 nm). The samples reported in the paper are listed in Table I. Scanning electron microscopy (SEM) imaging has been applied to study the morphology and growth dependent modifications of the Au NPs. Transmission electron microscopy (TEM) and associated analytical tools have been used to determine the structural and compositional properties of the nanostructures at a subnanometer scale. TEM samples were prepared using standard polishing techniques and Ar ion milling at 3kV.
2. Results and Discussion

2.1. SEM imaging
We have used the in-lens secondary electron detector of a Zeiss 1555 VPSEM, operating at low voltage. The SEM images of Au NPs grown on Si (111) at 60 °C show spherical NPs around 20 nm in size. Annealing at 600 °C maintains the surface morphology of the NPs grown at low temperature as revealed in figure 1a. As the growth temperature increases, the NPs begin to coalesce and different morphologies with larger, elongated NPs are observed at 400 °C (figure 1b). The deposition of Au NPs onto a different substrate also changes the morphology of the NPs. Au NPs deposited on silicon carbide exhibit lower surface Au coverage and variation in the Au NPs’ shape, including nanoparticles with different aspect ratios. This is possibly due to the different surface properties of the various substrates acting as a template for synthesis of the NPs.

![Figure 1](image1)

**Figure 1.** SEM images of Au NPs grown at low temperature and annealed at 600 °C (a), grown at high temperature (400 °C) (b); Au NPs on SiC grown at high temperature (600 °C) (c).

2.2. High resolution imaging
High resolution imaging (HREM) has been used to study the atomic structure of the nanoparticles and interfaces. The HREM study has been carried out using a JEOL 4010 TEM. The studies have shown that the nanoparticles are polycrystalline, with NP sizes in the range from 10-60 nm depending on growth conditions. For particles grown on the Si substrate, the interface between the NPs and the substrate was found to vary in thickness and composition depending on the deposition and annealing temperatures. The measurements of NPs and the NPs/substrate interfaces are summarized in table 1. A HREM image of a representative sample (grown at 60 °C and annealed at 600 °C) is shown in figure 2a. The HREM image shows the formation of an amorphous interface layer (confirmed by electron energy-loss spectroscopy (EELS) to be SiO$_2$, see below) 3 nm thick.

![Figure 2](image2)

**Figure 2.** (a) HREM and HAADF-STEM images of Au/Si interface along [112] Si. (b) STEM-EELS: (1)- Si substrate, (2) interface layer (SiO$_2$).

The interface layer may form due to air exposure and post-deposition oxidation of the Au/Si interface, since Au stimulates the oxidation of Si [8]. Figure 2a also demonstrates regions of considerably darker
contrast along the Si/SiO₂ interface (marked by arrows). This could suggest the presence of Au or a metastable Au₄Si (eutectic) phase at the Si surface. High-angle annular dark field scanning TEM imaging (HAADF-STEM) also revealed regions containing a high atomic number element present at the Si surface. This type of contrast was not observed in the samples as-grown at low temperatures. The formation of the SiO₂ layer is in agreement with extensive work on Au/Si interface formation that revealed Au-catalyzed silicon oxide formation by Au-induced Si bond breaking. The presence of Au at the silicon surface could result from out-diffusion of Au to the Si surface at high temperatures [9].

2.3. Analytical TEM

The chemistry of the nanostructures has been analysed using energy-filtered TEM (EFTEM), EELS and energy dispersive X-ray spectroscopy (EDS). The study has been carried out using a JEOL 3000F FEGTEM and an aberration corrected FEI Titan 80–300 TEM. EELS measurements across the interface confirmed the presence of the SiO₂ layer between the NPs and the substrate (figure 2b). To observe the elemental distribution within a Au/interface/Si stack, EFTEM images were acquired for the silicon L₂,3 edge, oxygen K edge, and gold O₂,3 edge and the optimum elemental mapping parameters calculated by use of a reference spectrum. The thickness of the oxide layers was estimated from a line profile across the layers using the full width at half maximum of the profile peak and was compared with the HREM measurements (see table 1). Figures 3a-d show an elastic image and EFTEM maps of the constituent elements. The EFTEM maps indicate that the oxygen is localized at the NPs/Si interface and demonstrate high surface roughness for the sample annealed at 600 °C. The interface thicknesses measured from HREM images and EFTEM data are shown in table 1. It was found that the interface thickness increased with deposition time and surface temperature. However, annealing of low temperature grown samples did not significantly affect the thickness of the interface layer. EFTEM profiles across the Au NPs/Si interface shown in figure 4a were correlated with STEM-EDS profiles shown in figure 4b. The interfaces between Au NPs and a substrate were found to be more stable at high temperatures when deposited onto SiC. TEM showed that synthesis of Au/SiC structures resulted in the formation of a reduced SiO₂ interfacial layer. It has to be noted that the SiO₂ layer was not present before NPs deposition as confirmed by in-situ ellipsometry. In all experiments the native oxide layer has been removed by chemical etching of the substrates before loading into the reactor. It could result from the post-deposition oxidation of the gold silicide interface, since gold silicides quickly oxidize.

| Table 1. Summary of HREM/EFTEM analysis of Au NPs and Au/substrate interfaces for 4 representative samples |
|---------------------------------------------------------------|
| Au/Si (111) @60 °C | Au/Si (111) @400 °C | Au/Si (111) Annealed @600 °C | Au/SiC @600 °C |
| NPs average size (lateral size/height) | 20/18 nm | 60/44 nm | 20/16 nm | 36/25 nm |
| NPs morphology | Spherical NPs | Elongated NPs | Spherical NPs | Elongated NPs |
| Interfacial SiO₂ thickness from HREM | 2.3 ± 0.1 nm | 6.1 ± 0.1 nm | 2.4 ± 0.1 nm | 2 ± 0.1 nm |
| thickness from EFTEM | 3.5 ± 0.5 nm | 6.9 ± 0.5 nm | 3.5 ± 0.5 nm | 2.9 ± 0.5 nm |
3. Conclusions
SEM analysis has shown that the Au NPs’ size and morphology varies as a function of growth conditions (temperature and substrate). Analytical TEM studies have revealed the formation of a SiO$_2$ interfacial layer in Au/Si and Au/SiC structures. An additional phase was observed at the Si surface in the samples grown/annealed at high temperatures that could be associated with the formation of a gold silicide phase.

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