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Silver endotaxy in silicon under various ambient conditions and their use as surface enhanced Raman spectroscopy substrates

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ABSTRACT

Search for reliable, robust and efficient substrates for surface enhanced Raman spectroscopy (SERS) leads to the growth of various shapes and nanostructures of noble metals, and in particular, Ag nanostructures for this purpose. Coherently embedded (also known as endotaxial) Ag nanostructures in silicon substrates can be made robust and reusable SERS substrates. In this paper, we show the possibility of the growth of Ag endotaxial structures in Si crystal during Ar and low-vacuum annealing conditions while this is absent in O_2 and ultra high vacuum (UHV) annealing conditions and along with their respective use as SERS substrates. Systems annealed under air-annealing and low-vacuum conditions were found to show larger enhancement factors (typically $\approx 5 \times 10^5$ in SERS measurement for 0.5 nM Crystal Violet (CV) molecule) while the systems prepared under UHV-annealing conditions (where no endotaxial Ag structures were formed) were found to be not effective as SERS substrates. Extensive electron microscopy, synchrotron X-ray diffraction and Rutherford backscattering spectrometry techniques were used to understand the structural aspects.

1. Introduction

Metal nano particles play a key role in many applications due to their high surface area availability and plasmonic properties. It is known that metal nano particles are good optical materials due to their surface plasmon resonance (SPR) properties. This surface plasmon resonance of the nanoparticles can be tuned by changing the shape, size and dielectric media around these nanoparticles [1,2]. Size, shape and density of the nano particles play a crucial role in SPR peak positions and surface enhanced Raman scattering (SERS) signal enhancement. Many optical applications are governed by the electron-relaxation rates that depend on the size of the nanostructures [3]. It is known that the quantum size and the chemical interface effect caused by static and dynamic charge transfer between a particle and the surrounding material would play an important role as well [3–11]. Among metal nano particles, silver has wide photonic applications due to its lowest on-resonance loss in the visible spectrum [4,12]. Embedded Ag nanoparticles were found to enhance the light absorption in the semiconductors, due to their strong plasmonic near-field coupling [12]. Recently, we reported on the growth of coherently embedded Ag nanostructures (also known as endotaxial structures) under ambient (in air annealing) conditions using chemical vapor deposition [13] and physical vapor deposition (PVD) [14]. For these endotaxial Ag nanostructures grown using PVD method, 3D imaging of coherently embedded structures and their applicability to use them as SERS substrate have also been reported [14]. Our present work is focused on understanding the role of ambience during annealing process and the substrate application as effective substrates for SERS—biomolecule detection. In this work, we report on the effect of ambience to understand the reaction processes at the interfaces in Ag/GeO_x/SiO_x/Si system by annealing it under various conditions, such as low vacuum, argon flow, oxygen flow, and ultrahigh vacuum (UHV) and the results would be compared to air-annealing case. By changing the ambient conditions, we show that the size, shape and position of silver nanostructures and surrounding matrix around these Ag nanostructures can get modified. Availability of oxygen appears to play a vital role in the reaction at the interfaces. A proper understanding of the growth of the endotaxial structure formation processes is still needs further controlled reactions at the interface. The present study is a step in this direction. A detailed characterization of resulting surface and interfaces has been carried out using field emission scanning electron microscopy (FESEM), transmission electron microscope (TEM), synchrotron X-ray diffraction (XRD) and Rutherford backscattering spectrometry experiments (RBS).

2. Experimental methods

Silicon (n-type, with 6–14 ohm-cm resistivity) wafers were cleaned by ethanol and ultrasonicated with ethanol for 10 min and rinsed with de-ionized water. A thin layer of ≈2 nm SiOx was found to be present

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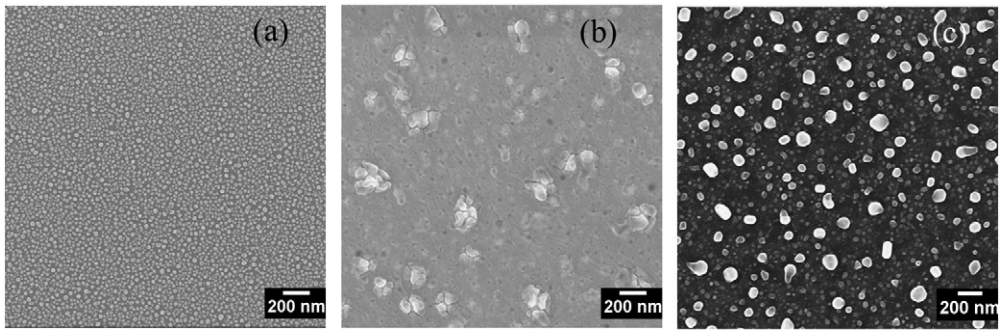

Fig. 1. SEM micrographs of 2 nm Ag/17 nm GeO_x/2 nm SiO_x/Si(100). (a) As deposited. (b) Annealed in oxygen. (c) Annealed in UHV at 800 °C for 30 min.

as native oxide (using cross-sectional TEM method). Deposition of GeO_x and silver was done by PVD process using a resistive heating boat in high vacuum condition. First, a ≈17 nm GeOx was deposited on Si(100), and was followed with further deposition of ≈2 nm Ag on 17 nm GeO_x/SiO_x/Si(100). This system consisting of 2 nm Ag deposited on 17nmGeOx/SiOx(native oxide)/Si(100) is henceforth represented as AGS.

It is interesting to note that, two earlier papers [15,16] reported on the reaction of oxygen on Ge surfaces at high temperatures. Law and Meigs observed that for all three faces (Ge(110), (111) and (100)), oxidation rates were inversely dependent on oxygen pressure at and above 550 °C and no differences in behavior between faces were observed [16]. Prabhakaran and Ogino reported on the formation and desorption of GeO and GeO_2 from the crystalline Ge (100) and Ge(111) wafers under very controlled conditions [17]. It is clear from these studies (and references in the above papers) that during the high temperature, Ge surfaces undergo oxidation and the grown oxide layer is volatile in nature at high temperatures. In our case, the Ge deposition was done in high vacuum conditions ($\approx 2 \times 10^{-3}$ Pa) using physical vapor deposition method. Crystalline wafers (Ge(111)) were used as source for deposition. The source material is expected to get oxidized while it is about to evaporate in the high vacuum environment due to the presence of residual oxygen molecules. This rate is much smaller when the Ge is heated in ambient conditions (atmospheric conditions). Law and Meigs report on how the Ge can be oxidized [16].

When the Ge substrate is heated, evaporation of GeO takes place and the rate of evaporation is proportional to temperature. For the deposition, Ge substrate is heated up to its melting point to get Ge vapors. During the heating of the Ge through molybdenum boat, above 550 °C, GeO vapors will produce. These vapors might contribute to the growth of GeO_x on the Si substrate along with Ge vapors produced through heating. There is a possibility of oxidation of Ge vapors during the transit from boat to substrate due to the presence of oxygen in the chamber. Partial pressure of oxygen for this vacuum is 4×10^{-4} Pa. These are might be reasons for the formation of GeO_x on the substrate during the deposition of Ge in physical vapor deposition.

Annealing of the samples at ≈800 °C was carried out in a side entry furnace with a quartz tube of 80 cm length and 5 cm diameter under different ambient conditions: (i) air, (ii) argon with a flow rate of 20 sccm, (iii) low vacuum of ≈1 Pa and (iv) oxygen with flow rate of 20 sccm and in (v) ultra high vacuum of $\approx 10^{-7}$ Pa using UHV chamber. Cross-sectional TEM (XTEM) samples were prepared by mechanical polishing followed by low energy Ar^+ ion milling to achieve the electron transparency. TEM measurements were carried out by using 200 keV electrons. Synchrotron X-ray diffraction (XRD) measurements were done at Photon Factory, KEK, Japan (at Indian Beam line 18B) with a wavelength of 1.089°A. RBS measurements were carried out using 3.0 MeV He^+ ions. Scanning electron microscope (SEM) measurements were carried out with 30 keV electrons using a field emitter gun based (FEG) SEM. Samples (2 nm Ag/17 nm GeO_x/SiO_x/Si(100) @ 800 °C) were cleaned using Piranha solution for 30 min and dipped in 5% hydrofluoric acid (HF) for 90 min to remove the top oxide layers. After removing from the HF solution samples were allowed to dry in air for 30 min and then CV solution was drop casted on top of the substrates. SERS spectra were recorded using micro-Raman spectrometer (LABRAM-HR) using laser excitation lines of 514.5 nm at room temperature and all the measurements were made in a backscattering geometry. 20 μl of the CV solution (5×10^{-10} M) was drop casted onto the SERS substrate and it was allowed to dry naturally. A fixed volume micro-pipette with disposable tips was used to prevent contamination. In our tests the dropped solution soon spread over the whole SERS substrate but remained confined to the substrate.

3. Results and discussion

The results of ambiance dependence are divided into two cases: (i) embedded spherical silver nanostructures formed in oxygen ambience, spherical nano structures in the case of UHV annealing, and (ii) substrate symmetric endotaxial silver nano structures formed in air, low vacuum and argon ambiences. Fig. 1(a) is the SEM micrograph of the as-deposited AGS specimen (i.e., 2 nm Ag/17nmGeO_x/SiO_x/Si(100)) depicting the irregular shaped silver islands. Fig. 2(a) depicts a low magnification XTEM image of as-deposited AGS revealing the position of silver nanostructures on top of ≈17 nm GeO_x layer on a native oxide covered silicon substrate.

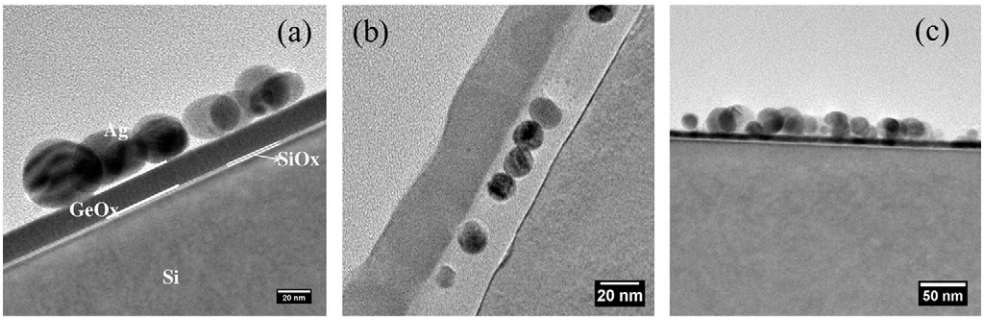

Fig. 2. X-TEM micrographs of 2 nm Ag/17 nm GeO_x/2 nm SiO_x/Si(100). (a) As deposited. (b) Annealed in oxygen. (c) Annealed in ultra high vacuum at 800 °C for 30 min.