Ion Irradiation Induced Effects in Metal Nanostructures

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ABSTRACT

High resolution transmission electron microscopy (HRTEM) and Rutherford backscattering spectrometry (RBS) are used to study the ion induced effects in Au, Ag nanostructures grown on Si and thermally grown SiO$_2$ substrates. Au and Ag films ($\sim 2$ nm) are prepared by thermal evaporation under high vacuum condition at room temperature (RT). These films were irradiated with MeV Au ions also at RT. Very thin films of Au and Ag deposited on silicon substrates (with native oxide) form isolated nano-island structures due to the non-wetting nature of Au and Ag. Ion irradiation causes embedding of these nanoislands into the substrate. For Ag nanoislands with diameter 15 - 45 nm, the depth of the embedding increases with ion fluence and the nano particles are fully submerged into Si and SiO$_2$ substrate at a fluence of $\sim 5 \times 10^{14}$ ions cm$^{-2}$ without any mixing. Au nanoparticles (diameter 6 - 20 nm), upon ion irradiation, forms embedded gold-silicide in the case of Si substrate and show lack of mixing and silicide formation in the case of SiO$_2$ substrate system.

Keywords: Au nanoparticle, Ag nanoparticle, MeV ion irradiation, gold-silicide, nano-scale ion beam mixing, embedding

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1 Introduction

As microelectronic devices and interconnects are reduced in size and electrical connections are made using ultra-low resistivity materials, many applications exist for noble metal thin films. On the other hand, energetic ion beams have been exploited in different ways in the field of materials science. The ion beam mixing is widely used for generating new phases specially silicides with the help of low energy ion beams. These phases have many potential applications in modern semiconductor industry for making contacts, interconnects, Schottky barriers, insulating layers, protective coatings, etc. [1, 2, 3]. Consequently ion beam modification of noble metal thin films has been an active area of research. Recently, this area has extended into modification of metal nanoparticles.

Energetic ion beams have been utilized in synthesizing and modifying nanostructures [4, 5, 6]. The application of ion beams to modify properties of nanomaterials has now become an important topic due to the emerging technological importance. As ion-irradiation is an athermal process, properties of nanomaterials could be modified where such modifications are not feasible by conventional methods [7]. The behavior of nanoparticles on surfaces is important for applications in catalysis, nanomagnetics, and optoelectronics. In most cases, nanoparticles are not thermodynamically stable on surfaces and would undergo smoothing reactions were it not for kinetic constraints. Nanoparticles that are immiscible with the substrate can undergo smoothing reactions by two mechanisms, wetting or burrowing [8]. When nanoparticles have surface energies that are sufficiently smaller than that of the substrate, they spread over the surface. When the surface energy is large, the nanoparticles tend to burrow. Ion-beam irradiation of Pt nanoparticles supported on a SiO$_2$ substrate leads to the burrowing of the particles into the substrate [9]. In other related studies on ion-induced effects in nanoislands, Baranov et al. [10] reported sputtering from nanoclusters with cluster ion beams. Among other effects induced by ion irradiation, sputtering of target atoms and modifications of target surface and interfaces are two important aspects. A radiation damage model that explains the production of interstitial atoms, vacant lattice sites, and displacement spikes was introduced several decades ago to understand irradiation effects in materials [11]. For ion-induced effects in target materials, the composition and morphological variations due to thermal spikes were investigated both experimentally [12, 13, 14, 15] and theoretically [16, 17, 18, 19, 20]. In our previous studies, we have reported about a push-in effect for silver nanoislands deposited on silicon substrates in comparison with gold nanoislands on silicon under MeV ion irradiation [21].
and absence of push-in effect in case of thick continuous Au film [22]. About 2 nm thick native oxide was present on the silicon substrate prior to film deposition. When a thin layer of SiO$_2$ is present on Si, the barrier formed at the metal SiO$_2$ interface is much higher than that obtained directly at the metal-semiconductor contact because of the large band gap of SiO$_2$. Here, we present results about push-in effect for gold and silver nanoislands deposited on silicon substrates with native oxide in comparison with gold and silver nanoislands deposited on a thermally grown SiO$_2$ substrate.

Ag and Au nanoparticles were selected for these experiments since noble metal nanoparticles on amorphous substrates such as SiO$_2$, have been widely used for heterogeneous catalysis. Moreover, Au and Ag are relatively inert in air, making possible ex-situ characterization of irradiated samples.

2 Experimental

Si wafers with native oxide (\(~2\) nm) and Si wafers with a thick (\(\sim 280\) nm) thermally grown SiO$_2$ layer were successively cleaned with trichloroethylene, acetone, and methanol in an ultrasonic bath and introduced into the thin film deposition chamber. Au (1.3 nm) and Ag (1.2 nm) films were deposited separately on such substrates by thermal evaporation at a rate of 0.1 nm/s. In the case of Au deposition was also carried out on HF-etched Si substrates. The chamber pressure during deposition was $8 \times 10^{-6}$ mbar. Irradiation was carried out with 1.5 MeV Au$^{2+}$ ions from the Peletron accelerator in our institute at an impact angle of 60$^\circ$ between the sample surface-normal and the incident ion beam and with fluences ranging from $5 \times 10^{13}$ to $5 \times 10^{14}$ ions cm$^{-2}$. The ion current for the irradiations was \(\approx 30\) nA and the ion beam was rastered over an area of $1 \times 1$ cm$^2$. During irradiation, $2 \times 10^{-7}$ mbar pressure was maintained in the irradiation chamber. Transmission electron microscopy (TEM) measurements were carried out with 200 keV electrons (JEOL JEM-2010). The cross-section and the planar samples were prepared using mechanical thinning followed by 3.0 keV Ar ion milling using a GATAN PIPS equipment. The amount of deposited material (the effective film thickness) was measured by Rutherford backscattering spectrometry using 2 MeV He$^{2+}$ ions.
3 Results and Discussions

Gold films of effective thickness $1.3 \pm 0.1$ nm on native-oxide/Si(100), HF-etched Si(100) and thermally grown SiO$_2$/Si(100) (denoted later as SiO$_2$/Si(100)) and silver films of thickness $1.2 \pm 0.1$ nm on native-oxide/Si(100) and SiO$_2$/Si(100) have been used for the present study. Gold and silver grow as nanoislands rather than uniform films. The amount of deposited material is expressed in terms of an effective thickness, which would be the actual film thickness if the film were deposited as a film of uniform thickness. The maximum height of the Au and Ag islands is $\sim 30$ nm. The range of the 1.5 MeV gold ions in Si at an impact angle of 60° is found to be $\approx 310$ nm using the SRIM 2003 range calculation [23]; the ranges of these ions in Au and Ag are $\approx 90$ nm and $\approx 120$ nm respectively. This means that ions, after interacting with the metal islands, get buried into the substrate.

3.1 Au/native-oxide/Si

TEM results from Au-deposited samples are shown in Fig. 1. Fig. 1(a) and (b) show plan-view TEM micrographs of an as-deposited and an ion-irradiated (fluence: $1\times10^{14}$ ions cm$^{-2}$) sample respectively. Gold islands are isolated with average particle size (diameter) $11.1 \pm 0.1$ nm, a standard deviation ($\sigma$) of $5.1 \pm 0.3$ nm and 26% surface coverage of islands. These values are obtained using several TEM micrographs and ImageJ analysis package. Fig. 1(c) shows a cross-sectional TEM (XTEM) micrograph of the sample shown in Fig. 1(b). From XTEM micrographs of an as-deposited sample, Au-island thickness (height) is found to vary mostly between 6 to 12 nm (data not shown). It is evident from Fig. 1(b) and 1(c) that craters are formed in Au nanoislands and Au has been embedded into the silicon substrate upon ion bombardment.

In order to understand more about the mixing and phase formation, we have carried out high resolution lattice imaging from the regions displaying buried structures. Fig. 1(d) shows such a high resolution XTEM (HR-XTEM) micrograph of a mixed region of Fig. 1(c) marked by a rectangle. The lattice image shows a d-spacing of $0.293 \pm 0.01$ nm. This value does not match with any of the inter-planar spacing in pure gold [19]. This value is very close to the (210) interplaner spacing of Au$_5$Si ($d_{210}$ for Au$_5$Si is 0.297 nm [24]). Results from RBS measurements are shown in Fig. 2, which presents spectra taken form pristine, ion-irradiated and aqua-regia-treated gold nanoislands on native-oxide/silicon substrate. We analyze these spectra based on the previous knowledge that aqua-regia removes Au by etching,
while it is unable to remove gold-silicide. The RBS spectrum from aqua-regia- treated pristine sample native-oxide/Au/Si shows the absence of gold signal, which is a natural consequence of etching of deposited Au by aqua-regia. RBS measurements on an aqua-regia-treated sample, following the irradiation with a fluence of $1 \times 10^{14}$ cm$^{-2}$, show the presence of almost as strong Au signal as it was before etching. As gold silicide cannot be removed by aqua-regia treatment, this indicates that at this fluence almost all Au form a reacted gold silicide either on the surface or within the silicon substrate. Considering these results together with the XTEM micrograph (Fig. 1(c)), it is clear that this gold-silicide is predominantly inside the silicon substrate. That is, ion bombardment has caused embedding of Au nanoparticles into Si and a concomitant reaction forming gold silicide.

### 3.2 Au/HF-etched-Si

Fig. 3(a) shows an XTEM micrograph of Au/HF-etched-Si substrate upon irradiation with an ion fluence of $1 \times 10^{14}$ cm$^{-2}$. From the micrograph it is evident that a band ($\sim 20$ nm) of reacted material forms at the sub-surface region. It should be noted that when Au deposited on a clean (without native oxide) Si substrate it wets more (data not shown) than that of Au deposited on native oxide layer atop the Si substrate. This may be understood from their respective surface free energies. Fig. 3(b) shows a high resolution XTEM micrograph of the region of Fig. 3(a) marked by a rectangle. The lattice image shows a d-spacing of $0.293 \pm 0.01$ nm. This value does not match with any of the inter-planar spacing available for the pure gold. This value again is very close to the (210) interplaner spacing of Au$_5$Si ($d_{210}$ for Au$_5$Si is 0.297 nm [24]).

### 3.3 Au/SiO$_2$/Si

For the Au nanoparticles grown on a thermally grown SiO$_2$, ion irradiation shows only embedding but no formation of gold-silicide. Fig. 3(c) shows an XTEM micrograph of ion-irradiated Au/SiO$_2$/Si (fluence: $1 \times 10^{14}$ cm$^{-2}$). From Fig. 3(c) it is evident that Au nanoislands are partially submerged into SiO$_2$ substrate. We perform lattice imaging from embedded region. One such image is shown in Fig. 3(d). The lattice image shows a d-spacing of $0.191 \pm 0.01$ nm. This value is very close to the (200) interplanar spacing of bulk Au ($d_{200}$ for Au is 0.203 nm). Inset in Fig. 3(d) showing FFT corresponding to region marked by a rectangle, displaying a [011] fcc diffraction pattern. These results confirm that the embedded part of the nanoparticle is unreacted Au.
3.4 Ag/native-oxide/Si

Fig. 4(a) shows XTEM micrograph of an as-deposited sample. From plan-view TEM images, the average particle size (diameter) for the Ag islands is found to be 31.6 ± 0.3 nm with σ = 14.3 ± 1.0 nm and with 22 % area coverage (data not shown). From XTEM micrographs, Ag-island height is found to vary between 10 to 30 nm. Fig. 4(b), (c) and (d) show XTEM micrographs of ion-irradiated Ag/native-oxide/Si with ion fluence of $5 \times 10^{13}$, $1 \times 10^{14}$ and $5 \times 10^{14}$ cm$^{-2}$ respectively. From Figs. 4(b)-(d) it is clear that depth of embedding increases with ion fluence and at a fluence of $\sim$ ions $5 \times 10^{14}$ cm$^{-2}$, the Ag nanoparticles are fully submerged into the Si substrate without any reaction. Fig. 5(a) shows an HR-XTEM micrograph of embedded Ag particle inside the Si matrix after irradiation with ion fluence of $5 \times 10^{14}$ cm$^{-2}$. The lattice image shows a d-spacing of 0.223 ± 0.01 nm, which is close to (111) interplanar spacing of bulk Ag ($d_{111}$ for Ag is 0.236 nm). Fig. 5(b), showing FFT corresponding to region marked by a rectangle in Fig. 5(a), displays a [011] fcc diffraction pattern.

3.5 Ag/SiO$_2$/Si

Fig. 5(c) shows an XTEM micrograph of Ag nanoparticles on SiO$_2$ after irradiation with ion fluence of $\sim$ ions $5 \times 10^{14}$ cm$^{-2}$. In this case also Ag nanoislands are fully submerged into SiO$_2$ substrate without any reaction. The HR-XTEM micrograph in Fig. 5(d) shows an embedded Ag particle inside SiO$_2$ matrix (magnified portion of Fig. 5(c) marked by a rectangle). The lattice image shows a d-spacing of 0.212 ± 0.01 nm, which is close to (200) interplanar spacing of bulk Ag ($d_{200}$ for Ag is 0.204 nm). The lattice spacing for Ag nanoparticles inside the Si or SiO$_2$ matrix could be somewhat different than bulk Ag lattice spacing.

4 Conclusions

We have shown that nanoparticles of Au and Ag on native-oxide-Si and on SiO$_2$/Si can be embedded into the substrates by ion bombardment. Not only just embedding, there is also a concomitant formation of a reacted material (gold-silicide) in case of Au/native-oxide-Si. The mixed phase of Au-Si is found to be crystalline in nature. No mixed phase formed in case of Au/SiO$_2$/Si, Ag/native-oxide-Si and Ag/SiO$_2$/Si. The high eutectic temperature, high and positive heat of mixing of Ag-Si system compared to the Au-Si system could be responsible for the lack of mixing in the Ag-Si system. If Co nanoparticles can be embedded into Si and an embedded nanoscale cobalt
silicide can be formed, it would be a prospective candidate for nanotransistors. As a Schottky barrier can be formed at the cobalt-silicide/silicon interface, depositing Si on this cobalt-silicide, in principle, a nanoscale metal base transistor can be fabricated.

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Figure captions:

Figure 1: (a) A plan-view TEM image from an as-deposited film showing Au nanoparticles on a native-oxide/Si substrate (b) Plan-view TEM image of Au nanoparticles on a native-oxide/Si substrate following 1.5 MeV Au\(^{2+}\) ion bombardment with a fluence of \(1 \times 10^{14}\) ions cm\(^{-2}\) at 60° impact angle; (c) An XTEM image of the sample in (b); (d) High resolution image from the region marked by a rectangle in (c).

Figure 2: RBS spectra form as-deposited, ion-irradiated and aqua-regia treated 1.3 nm Au/native-oxide/Si samples. Results confirm embedding of Au with concomitant silicide formation.

Figure 3: Cross-sectional TEM images of Au nanoparticles on HF-etched Si substrate and on thermally grown SiO\(_2\)/Si substrate irradiated with 1.5 MeV Au\(^{2+}\) at 60° impact angle: (a) Au nanoparticles on HF-etched Si substrate after irradiation with ion fluence of \(1 \times 10^{14}\) ions cm\(^{-2}\), (b) High resolution image from region marked by a rectangle in (a), (c) Au nanoparticles on SiO\(_2\)/Si substrate after irradiation with fluence of \(1 \times 10^{14}\) ions cm\(^{-2}\), (d) High resolution image of one embedded particle in (c). Inset in Fig. (d) Showing FFT corresponding to the region marked by a rectangle, displaying a [011] fcc diffraction pattern.
Figure 4: Cross-sectional TEM images of Ag nanoparticles on Si substrate irradiated with 1.5 MeV Au$^{2+}$ at 60$^\circ$ impact angle: (a) before irradiation, (b) after irradiation with ion fluence of $5 \times 10^{13}$ cm$^{-2}$, (c) ion fluence of $1 \times 10^{14}$ cm$^{-2}$, (d) ion fluence of $5 \times 10^{14}$ cm$^{-2}$.

Figure 5: (a) HR-XTEM images of Ag nanoparticles inside Si matrix after irradiation with 1.5 MeV Au$^{2+}$ at 60$^\circ$ impact angle, (b) showing FFT corresponding to region marked by a rectangle in (a), displaying a [011] fcc diffraction pattern, (c) Ag nanoparticles on SiO$_2$ after irradiation with ion fluence of $5 \times 10^{14}$ cm$^{-2}$, (d) HR-XTEM images of Ag nanoparticles inside SiO$_2$ matrix from a region marked by a rectangle in (c). The solid line drawn in (a) and (d) represents the surface.
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