Energy dependent sputtering of nano-clusters from a nanodisperse target and embedding of nanoparticles into a substrate

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ABSTRACT

Au nanoparticles, prepared by thermal evaporation under high vacuum condition on Si substrate, are irradiated with Au ions at different ion energies. During ion irradiation, embedding of nanoparticles as well as ejection of nano-clusters is observed. Ejected particles (usually smaller than those on the Si substrate) due to sputtering are collected on carbon-coated transmission electron microscopy (TEM) grids. Both the TEM grids and the ion-irradiated samples are analyzed with TEM. Unirradiated as well as irradiated samples are also analyzed by Rutherford backscattering spectrometry (RBS). In the case of low energy (32 keV) ions, where the nuclear energy loss is dominant, both sputtering and embedding are less compared to medium energy (1.5 MeV). In the high energy regime (100 MeV), where the electronic energy loss is dominant, sputtering is maximum but practically there is no embedding. Ion bombardment of surfaces at an angle with respect to the surface-normal produces enhanced embedding compared to normal-incidence bombardment. The depth of embedding increases with larger angle of incidence. Au nanoparticles after ion irradiation form embedded gold-silicide. Size distribution of the sputtered Au clusters on the TEM grids for different ion energy regimes are presented.

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1 Introduction

Sputtering from solids interacting with energetic particles is an active research area of great fundamental and applied interest. Momentum transfer to target atoms can be accomplished through elastic collisions or electronic processes. Linear collision cascade theory [1] has been used most successfully in describing the sputtering of metals by ions of keV energies. Enhancements due to elastic collision spikes are observed when both projectile and target consist of very high Z materials [2].

When an energetic particle passes into a solid, collisions induce several processes such as recoil and sputtering of constituent atoms, defect formation, electron excitation and emission, and photon emission. The sputtering process, especially emission process of secondary ions, has been widely studied for various target materials under bombardment of heavy ions. Most of studies are, however, concerned with secondary ion mass spectrometry (SIMS) at nuclear-collision dominant low energies [3-9]. In a MeV-energy range, an electronic-energy-loss process becomes dominant, [10] and the basic process of secondary ion emission is different from that in the low energy range because the electronic behavior strongly depends on the solid state property.

Birtcher et al. [11] reported ejection of nanoparticles from Au films that were irradiated with 50 - 400 keV Xe ions, providing evidence for pulsed plastic flow on the material structure. Rehn et al. [12] reported the size distributions of the large clusters (≥ 500 atoms) that are sputtered from the surface of thick films by high energy ion impacts (400 and 500 keV: Ne, Ar, Kr, and Au). They proposed that the clusters are produced when shock waves, generated by subsurface displacement cascades, impact and ablate the surface, as predicted in the model of Bitensky and Parilis [13]. Quite recently, a more representative set of data on sputtering of metal targets (Au and Ag films with thickness of ~1000 nm) with cluster ions of Au_n (n = 1-5 [14], n =1-13 [15]) with the energy from 20 keV/at. to 5 MeV/at. was obtained. Sputtering phenomenon can be expected to be considerably stronger in small finite systems like clusters [16][17][18]. The bombardment of Au clusters deposited on native-oxide/Si (100) surfaces has been investigated experimentally with ion energy and impact angle. Baranov et al. [17] reported sputtering of nanodispersed targets by 6 MeV Au_5 cluster ions (1.2 MeV/at.) and found that the size distribution of desorbed clusters are systematically shifted towards smaller sizes by comparison with the grain size distributions on the targets. Theoretical studies by Shapiro and Tombrello [19] showed that both the bal-
listic and thermal spike phases of collision cascades contribute significantly to the non-linearity and the large sputtering yields observed in the bombardment of gold targets with small gold clusters.

Ion beam mixing is a well-known technique for the formation of metastable and/or equilibrium phases in thin film structures [20-22]. The formation of silicides caused by the penetration of energetic ions through the interface between a metal-film and silicon has long back been recognized as one of the aspects of ion beam induced reactions in thin film structures [20, 21]. Lau et al. [22] reported about the ion beam mixing of four metal-semiconductor eutectic systems (Au-Si, Au-Ge, Al-Ge and Ag-Si). According to this report, for the Au-Si system, uniformly mixed amorphous layer with composition Au$_{71}$Si$_{29}$ was formed. These studies were on continuous thin films. For nanostructural islands (Au islands on Si) mixing can occur where ion range is much larger compared to the island thickness [23, 24].

Most of the above mentioned works were done where target films were continuous and projectile was monomer or cluster ion. We have done the measurements on nanodispersed target with monomer ion and the catcher grid being placed very far from target ($\approx$ 1 cm) at RT. This reduces the probability of agglomeration of nanoclusters coming out of the target and deposited on the catcher grid. We observe higher sputtering and higher probability of crater formation in nanodispersed gold target compare to thick semi-continuous and continuous target due to MeV self-ion irradiation and propose it as an experimental evidence of the energy spike confinement effect [18, 25]. An energy spike within the nanoislands which can result either in a thermal spike or a shock wave could see a spatial confinement effects in nanoislands. Kissel and Urbassek [16] studied theoretically the effect of 100 keV Au atom bombardment on spherical Au clusters (radius of 4 nm) using molecular-dynamics simulation and showed that this bombardment may result in total disintegration of the clusters.

## 2 Experimental

In this study, we use single crystal n-type Si(100) substrates (with native oxide of $\approx$ 2 nm). These substrates were cleaned sequentially in ultrasonic bath with acetone, methanol, trichloroethylene, methanol, deionized water and acetone. Au films of thickness 1.3 and 2.6 nm were deposited at a rate of 0.1 nm/s by thermal evaporation under high-vacuum conditions ($\approx$ 2 $\times$ 10$^{-6}$ mbar) onto Si at room temperature (RT). Ion sputtering experiments were
performed mainly with 1.5 MeV Au\(^{2+}\) ions with fluence of 1\( \times \)10\(^{14}\) ions cm\(^{-2}\) at different angles of incidence with respect to the surface normal. Supplementary studies done with 32 keV Au\(^-\) ions, and 100 MeV Au\(^{8+}\) ions. The ion current for the irradiations was \( \sim \) 30 nA for 32 keV and 1.5 MeV irradiation and \( \sim \) 15 nA for 100 MeV irradiation (under secondary electron suppressed geometry). To achieve uniform irradiation the ion beam was raster over an area of 1\( \times \)1 cm\(^{-2}\). During irradiation, 2\( \times \)10\(^{-7}\) mbar pressure was maintained in the irradiation chamber and sputtered particles were collected on a carbon coated TEM grid (catcher grid) that was positioned \( \approx \) 1 cm above the target and the catcher surface making an angle (\( \approx \) 15\(^{\circ}\)) with respect to the sample surface. 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. The amount of deposited material (the effective film thickness) was measured by Rutherford backscattering spectrometry (RBS) using 2 MeV He\(^{++}\) ions.

3 Results and Discussions

Gold initially grows as islands rather than uniform films on the native-oxide-covered Si substrates. 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 effective thickness has been determined by using the bulk atomic density of Au with RUMP simulation package [26]. The error on effective thickness determination was \( \leq \) 10\%. The maximum height of the Au island is \( \sim \) 30 nm. The particle size and the surface coverage have been determined from the TEM micrographs with the help of ImageJ software [27]. The amount of gold lost from the sample due to sputtering during irradiation has been calculated from RBS measurements. Projected range for Au ions in Si and Au for different ion energies is shown in Table 1.

Au films of thickness 1.3 nm and 2.6 nm was used for the present study. Fig. 1(a) shows a plan-view TEM image for as-deposited 2.6 nm Au films on native-oxide/Si substrate with 44% surface coverage of islands. Figs. 1(b), (c) and (d) show the TEM images of the sputtered particles collected from samples like the one shown in Fig. 1(a), which were irradiated with 32 keV, 1.5 MeV and 100 MeV Au ions, respectively, at a fluence of 1\( \times \)10\(^{14}\) ions cm\(^{-2}\) at normal incidence. From these figures, it is evident that in case of low energy (keV) ions, sputtering is less compare to high energy (MeV) in
Table 1: Projected range for Au ions in Si and Au for different ion energies (using the SRIM 2003 range calculation [28]).

| Au ion energy | Projected range in Si | Projected range in Au |
|---------------|-----------------------|-----------------------|
| 32 keV        | 23.4 nm               | 5.6 nm                |
| 1.5 MeV       | 360 nm                | 100 nm                |
| 100 MeV       | 14.7 µm               | 5.2 µm                |

this case (sputtering from nanoisland films). Fig. 1(e) shows a TEM image (from the same region as in Fig. 1(d)) from the catcher grid obtained by some underfocussing of the objective lens. The form of the image of the Au particles shows the spherical nature of the sputtered particles. Fig. 1(f) shows high resolution image of a sputtered particle obtained from Fig. 1(d). High resolution image shows crystalline nature of sputtered particles. Sputtered particles obtained for irradiation with 32 keV and 1.5 MeV are also crystalline and spherical in nature (data not shown).

The size distribution of the sputtered particles collected on catcher grids are shown in Fig. 2. The histograms shown in Figs. 2(a), (b) and (c) have been determined from many TEM images like Figs. 1(b), (c) and (d) respectively. Fig. 1(a) shows a bimodal size distribution for the sputtered particles with ≈2% surface coverage of islands for 32 keV ion irradiation. Fig. 1(b) shows monomodal size distribution for the sputtered particles with ≈14% surface coverage of islands for 1.5 MeV ion irradiation; here the mean size of islands is 7.5 ± 0.1 nm and standard deviation in size distribution is 3.7 ± 0.2 nm. Fig. 1(c) shows monomodal size distribution for the sputtered particles with ≈9% surface coverage of islands for 100 MeV ion irradiation; here the mean island size is 9.6 ± 0.1 nm and standard deviation in size distribution is 4.6 ± 0.2 nm. Though surface coverage of sputtered particles for 1.5 MeV ion irradiation is more (14%) than 100 MeV Au ion irradiation (9%) but average sputtered particle size is more for 100 MeV irradiation than 1.5 MeV irradiation.

Figs. 3(a), (b) and (c) show RBS spectra obtained from as-deposited 2.6 nm Au/Si and same samples irradiated with 32 keV, 1.5 MeV and 100 MeV Au ions respectively with fluence of $1 \times 10^{14}$ ions cm$^{-2}$ at normal incidence. Loss of Au from the sample due to sputtering can be estimated from these spectrum’s. RBS measurements showing more sputtering in case of 100 MeV Au irradiation by reducing the total Au signal and less sputtering in case of
32 keV Au irradiation compared to 1.5 MeV Au ion irradiation. From the RBS analyses we observe: (a) in case of 32 keV irradiation, the effective film thickness reduces from 2.6 nm to 1.5 nm upon ion irradiation (an effective reduction of 1.1 nm due to irradiation, i.e. an 42% thickness reduction (relative to the initial thickness), (b) in case of 1.5 MeV irradiation the effective film thickness reduces from 2.6 nm to 0.3 nm (an effective reduction of 2.3 nm occurred due to irradiation, i.e. a 88% thickness reduction), (c) in case of 100 MeV irradiation the effective film thickness reduces from 2.6 nm to 0 nm (an effective reduction of 2.6 nm occurred due to irradiation, i.e. a 100% thickness reduction). Obviously the sputtering yield is higher for 100 MeV ion irradiation. We have calculated relative sputtering yield (Y) for these ion energies from RBS measurements,

\[
Y \text{(at 32 keV)} : Y \text{(at 1.5 MeV)} : Y \text{(at 100 MeV)} = 1 : 2.1 : 2.4
\]

Figs. 4(a), (b) and (c) show XTEM images of 2.6 nm Au/native-oxide/Si, irradiated with fluence of \(1 \times 10^{14}\) ions cm\(^{-2}\) at 0\(^\circ\)-impact angle with 32 keV Au\(^-\) ions, 1.5 MeV Au\(^{2+}\) ions and 100 MeV Au\(^{8+}\) ions respectively. In case of 32 keV embedding is less compared to 1.5 MeV case. For 100 MeV, there is no embedding. We have seen very less sputtering in case of thick continuous film compare to island thin film [18].

Fig. 5(a) show the XTEM images of 1.3 nm Au/native-oxide/Si. Figs. 5(b), (c) and (d) show the XTEM images of such samples shown in Fig. 5(a) irradiated with 1.5 MeV Au ions at a fluence of \(1 \times 10^{14}\) ions cm\(^{-2}\) at 0\(^\circ\), 30\(^\circ\) and 60\(^\circ\)-impact angle, respectively. For this thickness there is no embedding for 0\(^\circ\)-impact and full embedding for 60\(^\circ\)-impact. Some embedding can be seen for 30\(^\circ\)-impact angle as well. From these results, we may infer that embedding is more for higher impact angles. However, we have not checked whether it is more or not if impact angle is higher than 60\(^\circ\). From the contrast near the silicon surface seen in Fig. 4(a), 4(b), 5(c) and 5(d) it appears that some Au has been pushed into silicon. In order to demonstrate that the contrast is indeed due to incorporation of Au into silicon, we have done aqua-regia treatment and carried out RBS measurements, which proves beyond doubt that indeed Au has entered into silicon [24].

To understand more about the mixing and phase formation, we have done high resolution lattice imaging from the mixed region (data not shown). The lattice image shows a d spacing of 0.224 ± 0.01 nm for pristine Au/Si (with native oxide) system, which is closer to (111) interplanar spacing of pristine and bulk Au ions. Upon irradiation with 32 keV and 1.5 MeV Au ions at a
fluence of $1 \times 10^{14}$ ions cm$^{-2}$ and at an impact angle of 0°, 30° and 60°, the lattice spacing is found to be $0.293 \pm 0.01$ nm. This value does not match with any of the interplanar spacing available for the pure gold. Thus, we conclude that this must belong to a metastable phase of Au/Si system. The mixed phase reported here is crystalline in nature [24].

From Figs. 4(b) and 5(b) it is evident that embedding of Au into Si at 0° largely depends on Au film thickness. From our earlier measurement [24] we have seen that for 0° as well as for 60°-impact there is no embedding in case of semi-continuous (94% film coverage) and in thick continuous Au film on Si for irradiation at a fluence of $1 \times 10^{14}$ ions cm$^{-2}$. In all the cases whenever there is a embedding (Fig. 4(a), 4(b), 5(c), 5(d)), embedded Au form a reacted material gold-silicide in the sub surface region.

4 Conclusions

We studied keV-MeV Au ion-irradiation effects on isolated nanoislands which were grown on Si substrates. We have collected sputtered particle on catcher grid. From TEM measurement sputtering is more in MeV energy region than keV region. RBS results confirm the effect through enhanced reduction in thickness for the film irradiated with 1.5 MeV and 100 MeV Au ions in comparison with that of 32 keV irradiation. We have provided an experimental evidence for an ion beam induced material push-in (or burrowing) for 32 keV and 1.5 MeV Au ion irradiation in nanoislands and nanosilicide formation in nano-Au/Si and its absence in case of 100 MeV irradiation. The formation of nanosilicide may be useful in fabricating embedded nanostructures such as nanocontacts and Schottky barriers. The embedding of nanoislands inside Si has been studied as a function of impact angle. Embedding is prominent at higher impact angles than at normal incidence.
References

[1] P. Sigmund, in Inelastic Ion-Surface Collisions, edited by N. H. Tolk, J. C. Tully, W. Heiland, and C. W. White (Academic Press, New York, 1977), p. 128.

[2] H. L. Bay, H. H. Anderson, W. O. Hofer, and O. Nielsen, Nucl. Instrum. Methods Phys. Res. 132, 301 (1976); P. Sigmund, Appl. Phys. Lett. 25, 169 (1974); ibid. 27, 521 (1975).

[3] L. Yu Ming, in R. Behrisch, and K. Wittmaack (Eds.), Sputtering by Particle Bombardment III, Springer, Berlin-Heidelberg, 1991, p. 91, and references cited therein.

[4] W. M. Lau, Nucl. Instr. Meth. B 16, 41 (1986).

[5] W. O. Hofer and H. Gnaser, Nucl. Instr. Meth. B 18, 605 (1987).

[6] D. van Leyen, B. Hagenhoff, E. Niehuis, and A. Benninghoven, J. Vac. Sci. Tech. A 7, 1790 (1989).

[7] R. Blumenthal, K. P. Caffey, E. Furman, B. J. Garrison, and N. Winograd, Phys. Rev. B 44, 12830 (1991).

[8] M. A. Karolewski and R. G. Cavell, Surf. Sci. 480, 47 (2001).

[9] S. F. Belykh, I. A. Wojciechowski, V. V. Palitsin, A. V. Zinoviev, A. Adriaens, and F. Adams, Surf. Sci. 488, 141 (2001).

[10] J. F. Ziegler, J. P. Biersack, and U. Littmark, The Stopping and Range of Ions in Solids, Pergamon Press, New York, 1985.

[11] R. C. Birtcher, S. E. Donnelly and S. Schlutig, Phys. Rev. Lett. 85 (2000) 4968.

[12] L. E. Rehn, R. C. Birtcher, S. E. Donnelly, P. M. Baldo and L. Funk, Phys. Rev. Lett. 87 (2000) 207601.

[13] I. S. Bitensky and E. S. Parilis, Nucl. Instr. Meth. B 21, 26 (1987).

[14] H. H. Andersen, A. Brunelle, S. Della-Negra, J. Depauw, D. Jacquet, and Y. Le Beyec, J. Chaumont and H. Bernas, Phys. Rev. Lett. 80 (1998) 5433.
[15] S. Bouneau, A. Brunelle, S. Della-Negra, J. Depauw, D. Jacquet, and Y. Le Beyec, M. Putrart, M. Callavier, J. C. Poizat and H. H. Andersen, Phys. Rev. B 65 (2002) 144106.

[16] Rolf Kissel and Herbert M. Urbassek, Nucl. Instrum. Meth. Phys. Res. B 180 (2001) 293.

[17] I. Baranov, A. Brunelle, S. Della-Negra, D. Jacquet, S. Kirillov, Y. Le Beyee, A. Novikov, V. Obnorskii, A. Pchelintsev, K. Wien and S. Yarmyychuk, Nucl. Instrum. Meth. Phys. Res. B 193 (2002) 809.

[18] B. Satpati, D. K. Goswami, S. Roy, T. Som, B. N. Dev and P. V. Satyam, Nucl. Instr. Meth. Phys. Res. B 212 (2003) 332.

[19] M. H. Shapiro and T. A. Tombrello, Nucl. Instrum. Meth. Phys. Res. B 152 (1999) 221.

[20] B. Y. Tsaur, S. S. Lau, and J. W. Mayer, Appl. Phys. Lett. 36 (1979) 168.

[21] J. M. Poate and T. C. Tisone, Appl. Phys. Lett. 24 (1974) 391.

[22] S. S. Lau, B. Y. Tsaur, M. von Allmen, J. W. Mayer, B. Stritzker, C. W. White, and B. Appleton, Nucl. Instr. Meth. Phys. Res. 182/183 (1981) 97.

[23] B. Satpati, P. V. Satyam, T. Som, and B. N. Dev, J. Appl. Phys. 96 (2004) 5212.

[24] B. Satpati, P. V. Satyam, T. Som, and B. N. Dev, Appl. Phys. A 79 (2004) 447.

[25] B. Satpati, D. K. Goswami, U. D. Vaishnav, T. Som, B. N. Dev and P. V. Satyam, Nucl. Instrum. Meth. Phys. Res. B 212 (2003) 157.

[26] L. R. Doolittle, Nucl. Instrum. Meth. Phys. Res. B 9 (1985) 344.

[27] http://rsb.info.nih.gov/ij/

[28] http://www.srim.org/
Figure Captions:

Figure 1: Plan-view TEM images: (a) as-deposited 2.6 nm thick Au film on native oxide coated silicon substrate; (b), (c) and (d) correspond to sputtered particles collected from samples (a), which were irradiated with 32 keV, 1.5 MeV and 100 MeV Au ions, respectively with a fluence of $1 \times 10^{14}$ ions cm$^{-2}$ at normal incidence ($0^\circ$-impact angle); (e) shows sputtered particles collected from the same region as in (d)) by some underfocousing of the objective lens; (f) shows high resolution image of a sputtered particle obtained after 100 MeV Au ion irradiation.

Figure 2: Size distribution of the sputtered particle collected on catcher grid following (a) 32 keV, (b) 1.5 MeV, and (c) 100 MeV Au ion irradiation with ion fluence of $1 \times 10^{14}$ ions cm$^{-2}$ at normal incidence.

Figure 3: RBS spectra obtained from as-deposited and ion-irradiated samples (at a fluence of $1 \times 10^{14}$ ions cm$^{-2}$ at normal incidence) for (a) 32 keV, (b) 1.5 MeV, and (c) 100 MeV Au ion irradiation.
Figure 4: XTEM images of ion irradiated 2.6 nm Au/native-oxide/Si with fluence of $1 \times 10^{14}$ ions cm$^{-2}$ at normal incidence: (a) 32 keV Au$^-$ ions, (b) 1.5 MeV Au$^{2+}$ ions and (c) 100 MeV Au$^{8+}$ ions.

Figure 5: XTEM images of 1.3 nm Au film on native-oxide/Si substrate following 1.5 MeV Au$^{2+}$ bombardment with ion fluence of $1 \times 10^{14}$ ions cm$^{-2}$: (a) as-deposited, (b) $0^\circ$-impact angle, (c) $30^\circ$-impact angle, (d) $60^\circ$-impact angle.
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