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Study of swift heavy-ion-induced modification in Ti/Si using x-ray standing waves

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Abstract

Intermixing in a Si/Ti/Si tri-layer induced by 120 MeV Au ions has been studied. X-ray standing wave analysis combined with x-ray reflectivity has been used to get a depth profile of the Ti marker layer with an accuracy of a fraction of a nanometer. Two different thicknesses of the Ti marker layer have been used to study the possible effect of layer thickness on intermixing. In the case of a 2 nm thick Ti layer intermixing is stronger as compared to a 6 nm Ti film, which can be understood in terms of a stronger confinement of the dissipated energy in the Ti layer due to increased interface scattering of δ -electrons in the case of the 2 nm thick Ti layer. In the 6 nm thick Ti layer, intermixing is asymmetric at the two interfaces, which may be due to a possible asymmetry in the interface structure in the as-deposited film itself.

1. Introduction

High energy heavy ion beams are well established as powerful tools for modifying the surfaces and interfaces at the nanometer scale [1, 2]. Low energy ion beams (having energies \sim keV/nucleon) have been used for several decades for surface modifications via ion implantation or ion-beam mixing [3]. More recently, material modifications produced by swift heavy ions (having energies \sim MeV/nucleon) have been a subject of great interest. From the application point of view swift heavy ions have several advantages over low energy heavy ions: (i) they can produce modifications up to a depth of several microns and (ii) low irradiation doses are sufficient to produce modifications and thus bombarding ions do not produce any substantial changes in the material composition. From the point of view of a basic understanding, while the mechanism for material modification in the keV energy range is rather well understood, in MeV energy range the mechanism of energy transfer from the electronic system (which absorbs energy from the incident ions via inelastic collisions) to atomic motion, especially in the case of metallic systems, and subsequent intermixing are not yet properly understood.

Many of the features of the swift heavy-ion-induced modifications in bulk metallic systems, like variation of the

threshold electronic energy loss S_e from metal to metal, radius of the latent tracks, etc, can be understood reasonably well using the thermal spike model [4]. According to this model, the passage of a swift heavy ion through the target material leads to ionization of the atoms in its wake, accompanied by ejection of the excited electrons known as δ -electrons. These electrons transfer part of their kinetic energy to the lattice via electron-phonon coupling leading to the formation of a thermal spike along the ion track. However, more subtle effects like those of heat of mixing, ion velocity, layer thickness, etc, are yet to be properly understood.

In thin films and multilayers swift heavy-ion-induced modifications are generally stronger as compared to bulk metals [5]. The difference has been attributed to the fact that, as the layer dimensions decrease, scattering of the δ -electron from the interfaces increases, resulting in decreased mobility of the electrons. Thus, the volume over which the electrons dissipate their energy decreases, leading to an increase in the peak temperature of the thermal spike. This may lead to a stronger intermixing at the interfaces. Since such effects are expected to be small, a study of possible layer-thickness-dependent intermixing requires measurement of the concentration profile of intermixed species with high accuracy.

X-ray fluorescence measurement under standing wave condition has been shown to be a powerful technique for

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elemental depth profiling [6]. The depth resolution of the technique can be further improved by making use of an x-ray waveguide structure [7–9]. In the present work, we have used an x-ray waveguide in order to study swift heavy-ion-induced intermixing in Si/Ti/Si tri-layers with different thicknesses of Ti layer.

2. Experimental details

Two multilayers having structure: substrate (float glass)/Pt (50 nm)/Si (15.4 nm)/Ti (2 nm)/Si (9.0 nm)/Pt (3.5 nm), designated as Ti2, and substrate (float glass)/Pt (50 nm)/Si (14.7 nm)/Ti (5.8 nm)/Si (8.7 nm)/Pt (3 nm), designated as Ti6, have been prepared using ion-beam sputtering. The base pressure in the chamber was 1.5×10^{-7} Torr during deposition. The Si/Ti/Si tri-layer constitutes the cavity of a planar waveguide structure formed by the top and bottom Pt layers. Waveguide modes can be excited in the cavity whenever the following condition is satisfied:

$$D = n\lambda/2 \sin \theta_i \quad (1)$$

where λ is the wavelength of the x-rays, θ_i is the angle at which the x-rays fall at the interfaces of the cavity, D is the thickness of the waveguide cavity and n is the order of the mode [7, 8]. X-ray reflectivity and x-ray fluorescence measurements were done using a Bruker AXS D8 Discover diffractometer using Cu $K\alpha$ radiation. Reflected x-rays were collected using a scintillation detector, while the Ti fluorescence from the sample was measured using an Amptek XR100T PIN diode detector (with an energy resolution of 250 eV) kept vertically above the sample. Raman measurements were performed on a Horiba JY HR800 micro-Raman system using a 488 nm argon laser as an excitation source and a CCD detector. Samples were irradiated with 120 MeV Au^{7+} ions at fluences of 1×10^{13} and 2×10^{13} ions cm^{-2} using the 15UD Pelletron at Inter-University Accelerator Centre, New Delhi, India.

3. Results and discussions

Figure 1 gives the normalized Raman spectra of Ti2 and Ti6 pristine and irradiated films in the spectral range 100–700 cm^{-1} . The spectra for different samples are shifted vertically for clarity. The Raman spectra of all samples exhibit four distinct features: a broad peak around 460 cm^{-1} , two rather overlapping peaks around 135 and 175 cm^{-1} and a broad feature around 315 cm^{-1} . The broad peak at 465 cm^{-1} matches rather well with that of amorphous Si [10]. The broad feature around 315 cm^{-1} represents second-order acoustic phonon scattering due to Si [11]. The peak around 135 cm^{-1} matches that of platinum silicide [12, 13], while that around 175 cm^{-1} may be attributed to titanium silicide [9]. In the film with a higher thickness of Ti layer (i.e. Ti6), the intensities of platinum silicide and titanium silicide peaks are lower than those in the Ti2 film. This may be because of scattering of the laser beam from the Ti marker layer. With increasing irradiation fluence, the height of the Si peak at 465 cm^{-1} keeps on decreasing, indicating intermixing of Si with Ti. The

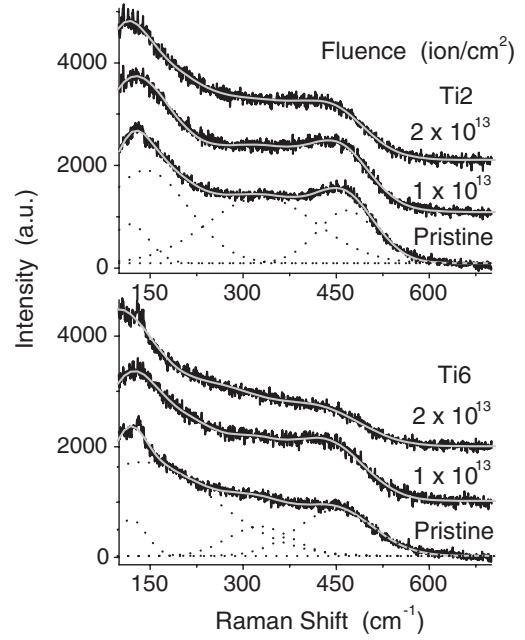


Figure 1. Raman spectra of Ti2 and Ti6 pristine and irradiated samples. The spectra for the different fluences have been shifted vertically for the sake of clarity. The continuous curves show the fitting of the data with four peaks, as discussed in the text. The dotted curves represent the four peaks corresponding to the pristine sample.

broad hump near 315 cm^{-1} , which is attributed to second-order acoustic phonon scattering due to Si, also decreases due to irradiation, which is in line with the arguments for decreasing the 465 cm^{-1} feature. The peak around 135 cm^{-1} suggests that, even in a pristine sample, some platinum silicide is formed.

Figure 2 gives the x-ray reflectivity and Ti fluorescence of Ti2 and Ti6 pristine samples as a function of scattering vector $q = 4\pi \sin \theta / \lambda$, 2θ being the scattering angle and λ being the wavelength of the radiation. Sharp dips in the x-ray reflectivity pattern below the critical angle for total reflection from Pt signals the excitation of waveguide modes. At the corresponding q values Ti fluorescence exhibits well-defined peaks due to resonance enhancement of x-ray intensity inside the cavity whenever a waveguide mode is excited.

The reflectivity and fluorescence data have been fitted simultaneously using Parratt’s formulation [14] in order to extract the thicknesses and roughness of various layers. The results of fitting are given in table 1. One notes that, while from the fitting of x-ray reflectivity the total thickness of the cavity can be determined very accurately, detailed information about the thickness and interface’s roughness of the marker layer is obtained from the fitting of the fluorescence data [9]. Thus, a simultaneous fitting of x-ray reflectivity and fluorescence data provides information about the thicknesses of various layers and their interface roughnesses with high accuracy.

Figure 3 gives the x-ray reflectivity and fluorescence of the Ti2 and Ti6 samples after an irradiation fluence of 1×10^{13} ions cm^{-2} . The concentration profile of the Ti marker layer in pristine as well as irradiated Ti2 and Ti6 samples is obtained by using the thickness and roughness parameter (table 1) assuming an error function profile at the interfaces.

Table 1. The results of simultaneous fitting of x-ray reflectivity and x-ray fluorescence data for pristine Ti2 and Ti6 samples, irradiated at a fluence of 1×10^{13} ions cm^{-2} . The given roughness is that of the top surface of a layer. Typical error bars in thickness and roughness parameters as obtained by simultaneous fitting of x-ray reflectivity and fluorescence data are 0.1 nm and 0.05 nm, respectively.

Layer	Ti2 pristine		1×10^{13} ions cm^{-2}		Ti6 pristine		1×10^{13} ions cm^{-2}	
	Thickness (nm)	Roughness (nm)	Thickness (nm)	Roughness (nm)	Thickness (nm)	Roughness (nm)	Thickness (nm)	Roughness (nm)
Pt	3.5 ± 0.1	1.0 ± 0.05	3.4 ± 0.1	1.6 ± 0.05	2.9 ± 0.1	1.5 ± 0.05	2.8 ± 0.1	1.7 ± 0.05
Si	9.0	1.6	8.2	2.2	8.65	1.8	7.0	2.1
Ti	2.0	0.8	4.0	1.4	5.8	1.7	7.6	2.3
Si	15.4	1.0	14.0	1.4	14.7	1.8	14.3	1.8
Pt	51.2	0.7	51.2	0.8	50.5	0.9	50.5	0.9
Substrate	—	0.2	—	0.2	—	0.3	—	0.3

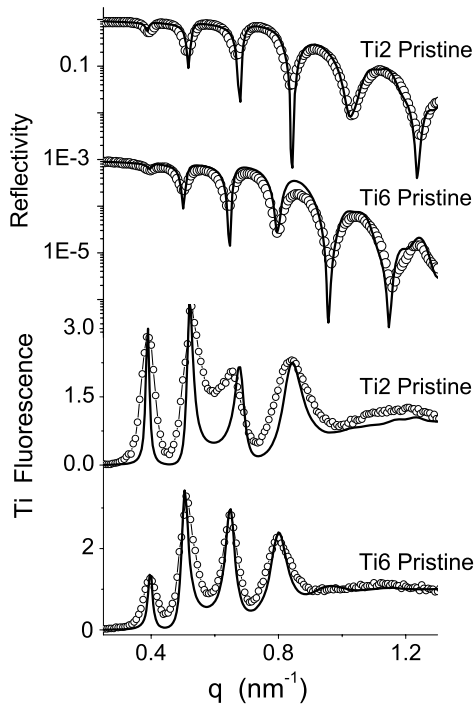


Figure 2. X-ray reflectivity and Ti fluorescence of Ti2 and Ti6 pristine samples as a function of scattering vector q .

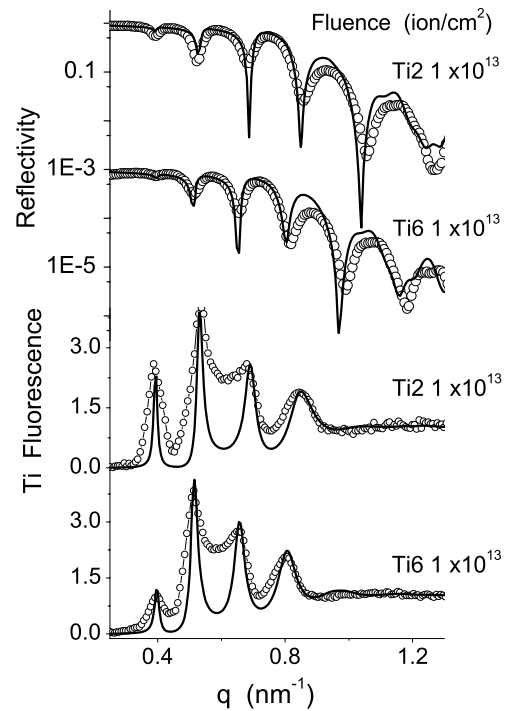


Figure 3. X-ray reflectivity and Ti fluorescence of Ti2 and Ti6 samples after an irradiation fluence of 1×10^{13} ions cm^{-2} as a function of scattering vector q .

The resulting concentration profiles are presented in figure 4. One may note that in both cases the concentration profile gets broadened as a result of irradiation. A Gaussian fit to the concentration profiles shows that in sample Ti2 the full width at half-maximum (FWHM) increases from 2.8 to 4.8 nm, while in sample Ti6 the width changes from 6.4 to 8.1 nm. Generally a quantitative estimate of intermixing is obtained using the relation [15]

$$\Delta\sigma^2(\phi) = \sigma^2(\phi) - \sigma^2(0), \quad (2)$$

where $\sigma(\phi)$ and $\sigma(0)$ are the standard deviation of the concentration profile before and after irradiation. However, this relation is valid only in the limit of a thin film solution, which is not valid in the present case. Therefore, only a qualitative statement can be made about the intermixing. Since in the case of the Ti2 sample the width of the concentration profile increases by 2.0 nm while in the Ti6 sample it increases by only 1.7 nm, intermixing is greater in the case of Ti2. This shows that in the case of a thicker Ti layer intermixing

is less compared to the thinner Ti layer, although irradiation fluence and ambient conditions are identical. The dependence of the magnitude of intermixing on the thickness of the Ti layer can be understood in terms of the thermal spike model. The incident Au ions lose their energy in the target primarily through electronic excitations, resulting in a high temperature of the electronic subsystem (δ -electrons) along the track of the ion. Part of the energy from the electronic system gets transferred to the lattice through electron–phonon coupling. This results in an increase in the temperature of the lattice along the ion track, which is termed the thermal spike. Transfer of energy from the δ -electrons to the lattice takes place at a timescale of 10^{-13} – 10^{-12} s. Temperature of the thermal spike thus generated depends upon the volume over which the energy imparted by swift heavy ions diffuses due to mobility of the δ -electrons over a time period of 10^{-13} – 10^{-12} s (1) and the strength of the electron–phonon coupling (2). Scattering of

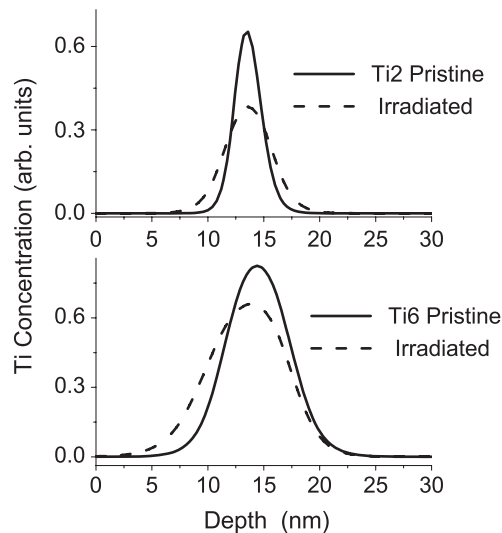


Figure 4. The concentration profile of the Ti marker layer in pristine as well as irradiated Ti2 and Ti6 samples, as obtained from simultaneous fitting of the x-ray reflectivity and fluorescence data.

the excited electrons from the film surface, various interfaces and also from the grain boundaries will reduce the mobility of the electrons. As the thickness of the Ti layer decreases the scattering of the δ -electrons generated inside the Ti layer at the interfaces will increase, resulting in a decrease in the mobility of the δ -electrons. Thus, in a film with smaller thickness the volume over which the energy of the δ -electrons gets distributed before the electron temperature comes down will be less and, as a result, the temperature of the thermal spike in this case will be higher compared to that in the case of a thicker film. This can explain the dependence of swift heavy-ion-induced mixing on the thickness of the Ti layer.

From figure 4 one may also note that in Ti6 samples the Ti concentration profile becomes skewed after irradiation. Thus the intermixing induced by swift heavy ions at the two interfaces Ti-on-Si and Si-on-Ti is not the same. More intermixing takes place at the Si-on-Ti interface as compared to the other one. The picture presented above on the basis of the thermal spike model cannot explain why the intermixing at the two interfaces of the Ti layer is different. In a number of studies on the multilayer it is found that the two types of interfaces, namely, a-on-b and b-on-a, have different structures [16]. For example, the Fe-on-Cr interface is more diffused as compared to the Cr-on-Fe interface. This can be because of the different surface energy of the two constituents [17]. A different structure of the two interfaces in the pristine samples themselves may be the cause of this asymmetric mixing at the interfaces. In the case of Ti2 sample, the thickness of the Ti layer is only 2 nm and even in the pristine sample Ti is almost completely mixed with Si.

4. Conclusion

In conclusion, 120 MeV Au ion-induced intermixing in an Si/Ti/Si tri-layer has been studied using x-ray reflectivity and fluorescence measurements. Complementary information

is obtained from Raman measurements. The tri-layer is embedded in a planar x-ray waveguide which enables one to get the concentration profiles of the Ti layer with sub-nanometer resolution. Measurements on such a tri-layer with different thicknesses of Ti provide clear evidence of the dependence of intermixing on the thickness of the Ti layer. Intermixing is greater in the case of a thinner marker layer. The result in general can be understood in terms of the thermal spike model according to which the reduced mobility of δ -electrons due to increased scattering from the interfaces of the Ti layer results in confinement of the energy dissipated by the bombarding ions to a smaller volume and thus to a higher temperature in the thermal spike region. An asymmetry in the mixing at the two interfaces of the Ti layer has been observed. A possible difference in the structure of the two interfaces in the pristine samples themselves may be the cause of this asymmetry in intermixing.

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