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Physicochemical variation of mica surface by low energy ion beam irradiation

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ABSTRACT

We report the transformation of smooth and hydrophilic mica surface to a patterned and hydrophobic surface by 12 keV Ar^+ and N^+ ion bombardment at oblique ion incidence. Periodic ripple pattern has been found on the mica surface when nitrogen like lighter or argon like heavier ions are bombarded at an angle 60° with respect to the surface normal. During ion bombardment the different components of multi-elemental mica are eroded at different rate; as a result surface chemistry is changed, as well as a surface ripple pattern is developed on the surface due to the generation of surface instabilities. The change of surface chemistry and presence of pattern change the hydrophilic nature of the mica surface. X-ray photoelectron spectroscopy (XPS) study of irradiated mica surface shows that the upper K atoms are sputtered most. The vertical and lateral dimensions of the surface patterns are controlled by varying the ion fluence. Contact angle measurement of un-irradiated and irradiated mica surface shows a certain change from hydrophilicity to hydrophobicity. The physicochemical changes of mica surface due to Ar^+ and N^+ ion bombardment have been discussed.

1. Introduction

Muscovite mica is a naturally occurring mineral, which is endowed with the peculiar features of being a good conductor of heat but a poor conductor of electricity, it also posses high-dielectric properties. Mica is also important due to its layered structure consisting of negatively charged alumino-silicate sheets that are bound to alternating layers of K^+ ions [1,2]. It can thus be easily cleaved which yields an atomically flat surface. High quality of mica sheet is available and it is widely used as a substrate for various applications related to scanning probe microscopy, biotechnology and materials science [3–8]. Recently, the use of mica in nanoscale bio science has been increased enormously for its easily available atomically flat smooth surface. Mica is also used as a substrate in the production of ultraflat thin-film surfaces. Freshly-cleaved mica surfaces have been used as clean imaging substrates in atomic force microscopy [9], enabling, for example, the imaging of bismuth films [10], plasma glycoproteins [11], membrane bilayers [12], and DNA molecules [13] .

The presence of regular nanopattern with controlled hydrophilic properties is highly desired for various applications from supported lipid bilayer membrane, thin film deposition, to synthesis of organic functional materials [14,15]. The change of hydrophilic nature of mica surface is very important for the study of interactions between surface, bio membrane and proteins [16,17]. Although the research work on muscovite mica is limited, the study on mica crystals is a great interest for more than two decades by heavy ion irradiation [18]. F. Thibaudau et al. [18] observed the formation of latent tracks in mica surface induced by swift Kr^+ ions. The nanoscale hillocks formation by highly charged ion on mica attracted more attention [19]. Recently, very low energy (eV) ion beam induced nano patterning and hydrophobic nature of mica surface have been reported [1,20]. Buzio et. al. [21] also showed the ripple structure of the mica surface by 1.04 keV Ar^+ ion sputtering at an incidence angle of 35°.

In this paper, we report the surface chemical change and nano-ripple pattern formation on mica surface by 12 keV Ar^+ and N^+ ions beam. Differential sputtering of surface elements by keV energy ion beams alters the chemical nature of the surface and also develop regular nano patterns. We study the growth of surface morphology with fluence of Ar^+ and N^+ ions at an oblique angle (6 0°). We also examine the hydrophilic to hydrophobic transition of mica surface due to keV energy lighter and heavier ion bombardment.

2. Experimental

Freshly cleaved mica samples were irradiated at an oblique angle 60° with 12 keV Ar^+ and N^+ ion beams. The Ar^+ and N^+ ion beams were extracted from a 2.4 GHz ECR based ion beam system at Variable Energy Cyclotron Centre (VECC), Kolkata. The beams were mass

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analyzed by a dipole magnet and collimated to get a uniform beam of 8 mm diameter on the surface. The samples were surrounded by a cylindrical cup with 90 V negative bias which suppresses the secondary electrons from the sample. The base pressure in the target chamber was around 1×10^{-7} mbar and it was 5×10^{-7} mbar during the ion beam experiment. The morphology of virgin and irradiated mica samples was carried out in air using Bruker Atomic Force Microscopy (AFM), Multi-Mode V at VECC, Kolkata.

The X-ray photoelectron spectrum (XPS) of virgin and irradiated mica samples were measured using an Omicron Multi-probe (Omicron Nano Technology, UK) ultrahigh vacuum(UHV) system (base pressure ~ 5.0×10^{-10} mbar). A monochromatic Al K_α source was used to provide photons of energy 1466.6 eV for XPS measurement. The contact angle measurements were carried out in a standard contact angle goniometer (ramé-hart model 250, USA) with DROPimage Advanced v2.4 software. The sessile drop method was used for this measurement. The contact angles were measured at least on five different spots for each sample and the average values were taken. During measurements, the room temperature was in the range 20–24°C and the relative humidity was 45–47%.

3. Results and discussions

Fig. 1 shows the AFM images of virgin mica, and 12 keV Ar^+ ion irradiated mica surfaces at oblique angle incidence. The fluences of the ion beam were varied from 3×10^{17} to 1×10^{18} ions/cm^2. From AFM morphology, it is observed that the virgin mica is flat with very low roughness ~ 0.7 nm. After the bombardment, the rms roughness of the mica surface is increased and a periodic ripple pattern is formed. Similar ripple pattern formation on mica surface by lower energy (500 eV) Ar^+ ion bombardment was also reported earlier [20]. The inset of the AFM images is the Fast Fourier Transform (FFT) images which show that the ripple wavevector is oriented parallel to the ion beam direction. The variation of rms roughness and ripple wavelength obtained from AFM images are shown in the Fig. 2. From the variation, it is clear that both the surface roughness and ripple wavelength increase with incident ion fluence.

To observe the pattern formation on mica by relatively lighter ion, we have bombarded the mica surfaces by 12 keV N^+ ion beam at the same oblique incidence (60°) for three different fluences. Regular ripple patterns were observed (shown in Fig. 3). The variation of rms roughness and ripple wavelength with ion fluence are also shown in Fig. 3(d) and 3(e), respectively. Both the rms roughness and ripple wavelength increase with the ion fluence.

The ripple patterns are formed on the ion bombarded surface due to the generation of surface instabilities [22–24]. The instabilities are generated during ion bombardment due to initial perturbation on the surface [25], presence of contamination [26], unequal sputtering [27], redistribution of surface atoms [23,28] and local curvature dependent sputtering [29]. In the present case, mica is a multi-elemental compound. When the ion beams are bombarded on crystalline mica, it loses its crystalline property as well as sputters the different elements at different rate. Due to the preferential sputtering and re-arrangement of atoms the regular ripple patterns are formed.

It is observed for both Ar and N ion bombardment that at higher fluence (Figs. 1g and 3b,c) the continuous ripples are broken and formed a pattern which is a combination of dot and ripple. Preferential sputtering of mica like compound target leads to the enrichment elements having lower sputtering yield. Our XPS measurement (Fig. 4) shows enrichment of Si and Al compared to K and O. Such ripple breaking at higher fluence may be due to the higher enrichment of elements. Instead of ripple, nanodot formation on oblique ion sputtered InP surface was reported earlier [30]. Further, relatively higher enrichment of Si is observed for nitrogen bombardment compared to argon. Therefore, we found breaking of ripple structure at earlier fluence for nitrogen bombardment (Fig. 3), compared to Ar (Fig. 1).

Fig. 4 shows the schematic of crystalline mica structure, and XPS spectra of virgin, 12 keV Ar^+ and N^+ bombarded mica surfaces for ion fluence of 5×10^{17} ions/cm^2. The chemical composition of mica is $[KAl_2(Si_3Al)O_{10}(OH)_2]$. The X-ray photoelectron spectra (XPS) of cleaved virgin mica shows the presence of all the elements (Fig. 4b). Buzio [21] et al. and Bhattacharyya et al. [31] also showed the presence of all the elements on the virgin mica surface. Mica being a multi-layered and multi-elemental compound, the surface can be chemically modified by ion beam bombardment. When keV energy ions are bombarded on the cleaved mica surface, the chemical composition is immensely changed. To observe the effect of post bombardment by lighter ions (N) and heavier ions (Ar), the XPS spectra of mica surface after the 12 keV Ar^+ and N^+ ion bombardment are recorded and also shown in Fig. 4 (b). Different elements of the mica surface are eroded at different sputtering rate during ion bombardment. The surface concentrations of all elements at atomic % for virgin as well as 12 keV N and Ar bombarded mica surfaces are shown in Fig. 4c. We have calculated the sputtering yield of different elements of mica surface by the Monte Carlo code Transport of Ions in Matter (TRIM) [23] considering the actual stoichiometric ratio of the elements (Fig. 5). It is found that the

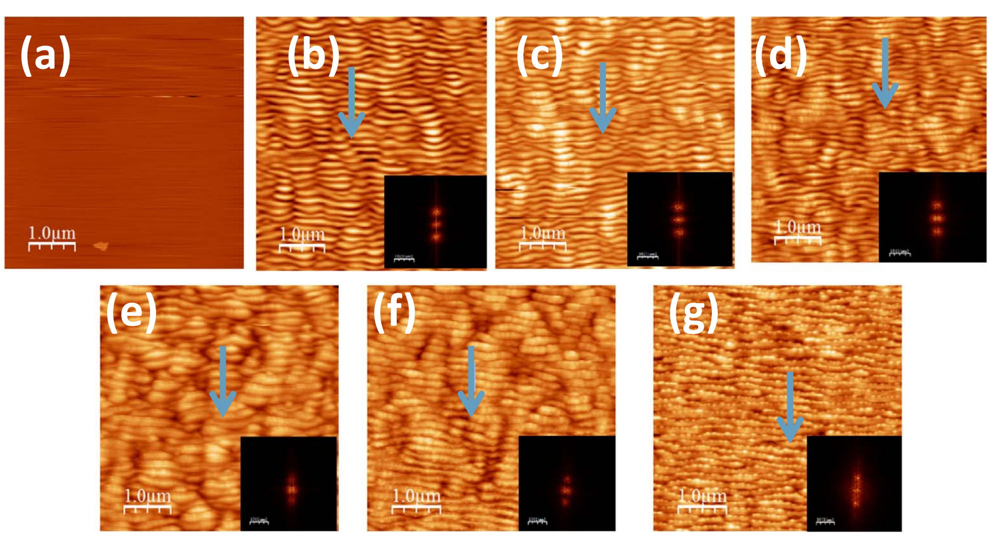

Fig. 1. AFM images of (a) virgin and 12 keV Ar^* bombarded mica surface at oblique incidence with fluence (b) 3×10^{17}, (c) 5×10^{17}, (d) 6×10^{17}, (e) 8×10^{17}, (f) 9×10^{17}, (g) 1×10^{18} ions/cm^2. The FFTs ($50\,\mu m^{-1} \times 50\,\mu m^{-1}$) are shown in the corner of each AFM images. The arrows indicate the ion beam direction.