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Morphological study of magnetron sputtered Ti thin films on silicon substrate

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ABSTRACT

Titanium films on Si(1 0 0) substrate were deposited by DC-magnetron sputtering. The effect of substrate temperature on the microstructural morphologies of the films was characterized by using field emission-based scanning electron microscopy/electron back scattered difffraction (FE-SEM/EBSD) and atomic force microscopy (AFM). X-ray diffraction was used to characterize the phases and crystallite size of the Ti films and it was observed that according to the first figure of this article: (0 0 2) orientation increases from 200 °C and it changes into (1 0 1) orientation from 300 °C. The SEM analysis of the Ti films, deposited in Ar atmosphere, showed two- and three-dimensional hexagonal structure of the grains at the substrate temperature of 200 °C and >200 °C, respectively. The increase in grain size of Ti films with the substrate temperature was confirmed by EBSD and AFM characterization. The average surface roughness of the Ti films has increased with increase in substrate temperature as evident from the AFM study.

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1. Introduction

Titanium (Ti) exhibits high mechanical strength, excellent thermal stability, good corrosion resistance in extreme conditions and intrinsic biocompatibility. It finds extensive use for the structural and functional applications, especially in biomedical, aerospace, and microelectronics industries [1–5]. The properties of Ti thin films deposited by physical vapor deposition techniques are heavily dependent on their microstructural characteristics such as grain morphology, textures, and porosity. It is possible to tailor the properties of Ti films through the nanoscale features of the grains achievable by accelerating the nucleation kinetics during the sputtering process.

Bunsha and Juntz [6] investigated the influence of substrate temperature on the microstructure of Ti films deposited by high rate physical vapor deposition. They observed very fine and fine columnar morphology α at 450 °C and 740 °C, respectively. The whisker and coarse columnar α morphologies were observed at 840 °C and between 850 °C and 883 °C, respectively. The β phase has been observed at the temperature above 883 °C.

Naeem et al. [7] investigated the influence of deposition temperature on the grain size of Ti films and reported the reduction in grain size with decreasing substrate temperature [8]. Masahiko Naoe et al. [9] investigated the various sputtering conditions such as the argon pressure, the substrate temperature and the bias voltage, on Ti films and found that more or less hcp, crystallites with $(0 1 \bar{1} 0)$, (0 0 0 2) and $(0 1 \bar{1} 1)$ orientations parallel to the film plane and amorphous-like fine grains were manifested in the films. The reduction of Ar pressure has deteriorated the crystallinity and the (0 0 0 2) orientation, but produced a smooth surface and dense morphology. The well-oriented (0 0 0 2) films with smooth surface and columnless structure were obtained by means of the deposition of initial layer with high (0 0 0 2) intensity and at the higher substrate temperature. The application of bias voltage has damaged the crystallinity and developed the $(0 1 \bar{1} 0)$ and $(0 1 \bar{1} 1)$ orientations although the smooth surface and dense morphology was obtained at a moderate bias voltage in their work. The DC magnetron sputtered Ti films deposited on TiNi shape memory was characterized by SEM and observed that the films exhibit uniform thickness morphology and adherent to the substrate [10].

The surface morphology of the titanium films has gradually changed from the structure consisting of fine particles to that of fine fibers with increase in substrate temperature. XRD analysis of the films showed the presence of α-titanium phase with the (0 0 2) orientation increasing up to the substrate temperature of 320 °C. However, the (0 1 1) orientation gets increased while the (0 0 2) orientation diminished at a higher temperature range. The fine particles yielded the (0 0 2) peak while the fine fibers yielded the (0 1 1) peak [10]. Jeyachandran et al. [5] characterized DC magnetron sputtered Ti thin films on Si(1 0 0) substrates by using XRD,

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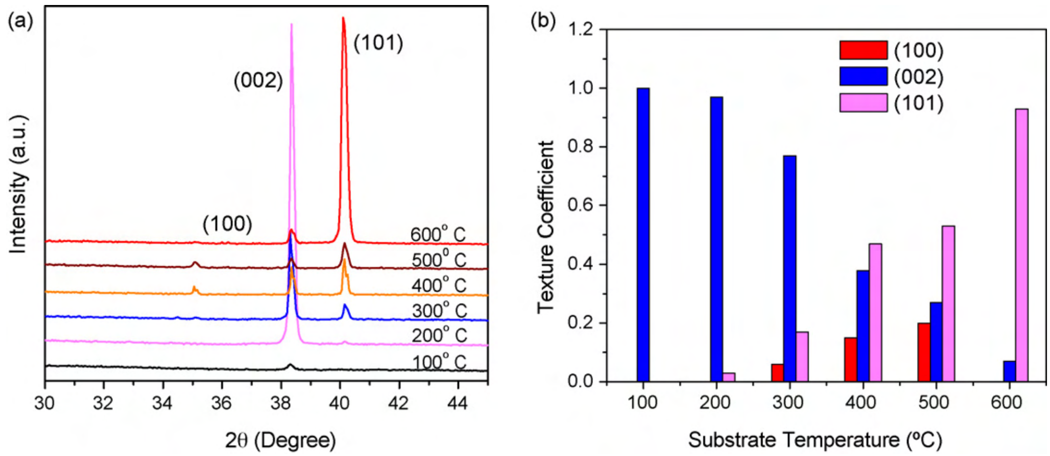

Fig. 1. (a) XRD peaks of Ti films deposited on SILICON substrate as a function of substrate temperature in argon atmosphere and (b) texture coefficients of the same samples.

SEM, spectroscopic ellipsometry technique. The films were found to be uniform, void free and dense morphology. Its preferred orientation was (0 0 0 2), from the XRD study, at the 100–150W cathode power. The similar morphologies of the Ti thin films were observed by Jung et al. [11–14] investigated the growth of ultrathin Ti films deposited on SnO_2 by magnetron sputtering and observed the formation of three-dimensional particles and layer by layer structures following the Volmer weber and Frank van der Merve mode of growths, respectively. The Ti films deposited using pulsed magnetron sputtering were characterized in terms of optical properties, microstructure, and mechanical properties by Henderson et al. [15]. They reported the formation of smooth film morphology and heavily pitted surface at the frequencies of 100 kHz and 350 kHz, respectively. The effect of bias power on the growth morphology of Ti films prepared by RF magnetron sputtering was studied by Martin et al. [16] and they observed the cleaning action, knocking, and resputtering of the forming film, for the weak bias, intense bias (300 W), and above 300 W, respectively. The films composed of spherical nodules of about 60–80 nm in diameter, which are coalescent and distinguishable under the deposition conditions without bias power.

The influence of various process parameters such as substrate temperature, pressure and power on the morphological features of Ti films needs to be thoroughly understood for its superior performance and reliability in the actual device applications. Owing to this view, the present work has been focused to produce Ti films on Si substrate by DC-magnetron sputtering at different temperatures and characterize their microstructural features by XRD, SEM/electron backscatter diffraction (EBSD) and atomic force microscopy (AFM).

2. Experimental details

2.1. Processing of Ti films

The Ti films were deposited by DC-magnetron sputtering on silicon (1 0 0) substrates from a 99.99% pure titanium target (2-in. diameter and 5-mm thick). The substrates were cleaned by rinsing in ultrasonic baths of acetone and methanol and dried under nitrogen gas. The base pressure was better than 2×10^{-6} Torr and the sputtering was carried out in an Argon atmosphere. The ambient argon gas pressure was kept at 10 mTorr for all depositions. Before starting the actual experiment, the target was pre-sputtered for 15 min with a shutter located in between the target and the substrate. This shutter was used to control the deposition time. The target-substrate distance was kept at 50 mm. The Ti films were deposited at fixed sputtering power of 100 W with different substrate temperatures ranging from 100 °C to 600 °C. The deposition time was kept constant for all depositions.

2.2. Characterization details

The Ti films were characterized by XRD (Bruker AXS) with Cu Kα radiation for the phase identification, grain size measurement and texture analysis. The scan rate used was 1° min^{-1} and the scan range was from 30° to 45°. The surface topographical characterizations of the Ti films were obtained from SEM (FEI, Quanta 200F) at an acceleration voltage of 20 kV. The surface morphology of the Ti films was studied using AFM (NT-MDT, Ntegra) operated in semicontact (tapping) mode. The electron backscatter diffraction was used to obtain the grain size distribution of Ti films.

3. Results and discussion

XRD peaks of Ti films deposited on the Si (1 0 0) substrate in Ar atmosphere at different substrate temperatures ranging from 100 °C to 600 °C are shown in Fig. 1(a). It was found that the intensity of the (0 0 2) reflection of the films increases with increase in the substrate temperature around 200 °C. With further increase in temperature above 200 °C, the (0 0 2) orientation subsides while (1 0 1)

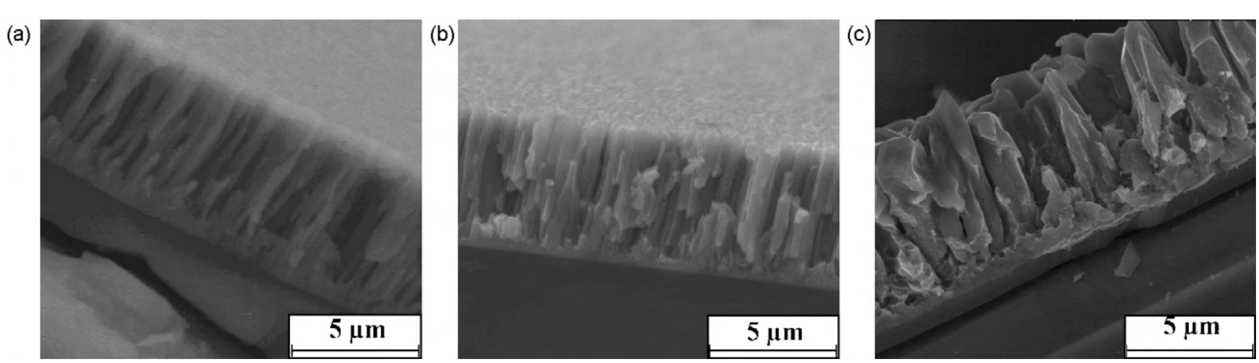

Fig. 2. Cross-sectional view of titanium film on silicon substrate deposited at substrate temperature: (a) 200 °C, (b) 400 °C and (c) 600 °C.

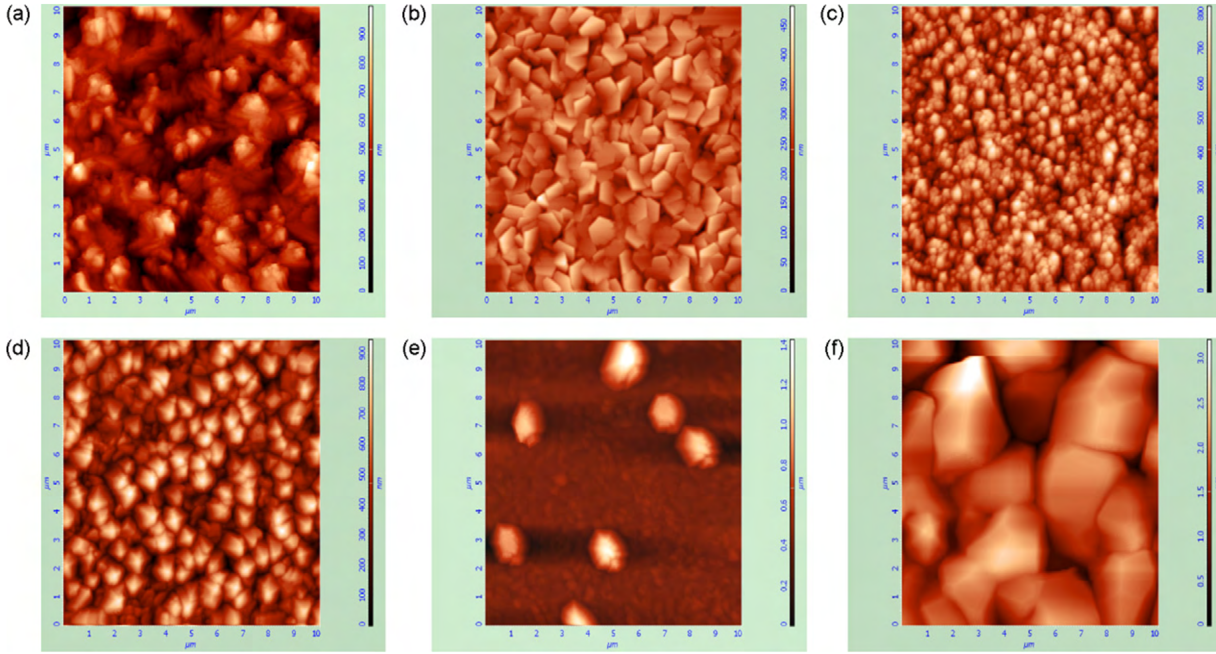

Fig. 3. AFM images of titanium films on silicon deposited at substrate temperature: (a) 100 °C, (b) 200 °C, (c) 300 °C, (d) 400 °C, (e) 500 °C and (f) 600 °C.

orientation dominates. With the increase in substrate temperature the crystallite size also increases as expected from 40.75 nm at 100 °C to 57.75 nm at 600 °C, however (0 0 2) orientation transformed into (1 0 1) preferred orientation. The enhanced mobility of adatoms in the film surface with the increase in substrate temperature has favoured the formation of (1 0 1) orientation of grains. The competition between strain energy and surface free energy affecting the texture of the grains are heavily dependent on the deposition parameters such as substrate temperature, power, sputtering pressure and film thickness. The thermal stress induced in the thin films deposited at higher substrate temperature might have also contributed to the modification of (0 0 2) preferred orientation, favouring the formation of (1 0 1) grains. The texture coefficients of Ti films as a function of substrate temperature were calculated from its XRD peaks using the following formula and shown in Fig. 1(b).

$$\text{Texture coefficient } (T) = \frac{I(h\,k\,l)}{I(1\,0\,0) + I(0\,0\,2) + I(1\,0\,1)} \quad (1)$$

where $h\,k\,l$ represents (1 0 0) or (0 0 2) or (1 0 1) orientation [17]. The texture coefficients of (0 0 2) and (1 0 1) orientation are high as compared to other orientations in the Ti films deposited under Ar atmosphere. It is clear that the higher deposition temperature

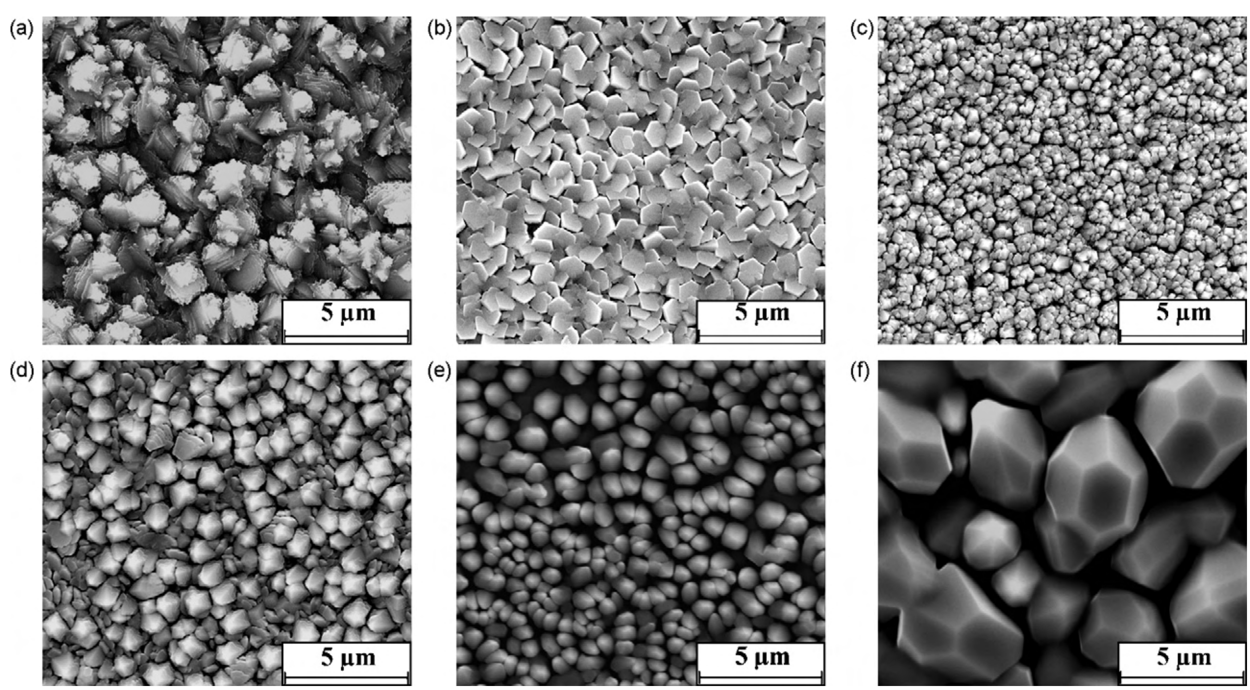

Fig. 4. FE-SEM images of titanium films on silicon deposited at substrate temperature: (a) 100 °C, (b) 200 °C, (c) 300 °C, (d) 400 °C, (e) 500 °C and (f) 600 °C.

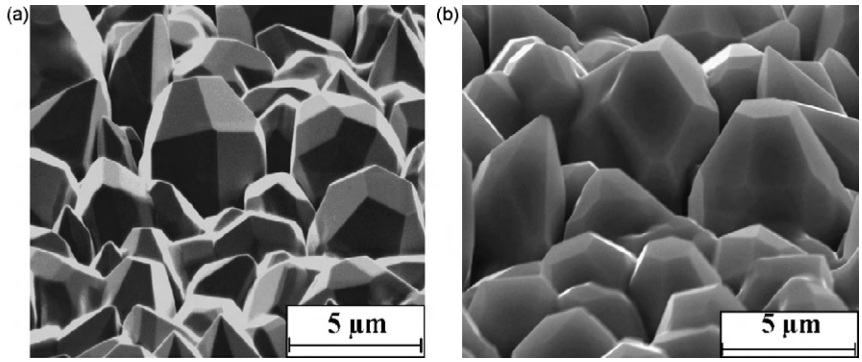

Fig. 5. Tilted FE-SEM images of Titanium films on silicon deposited at substrate temperature 600 °C: (a) HV = 3 kV and (b) HV = 20 kV.

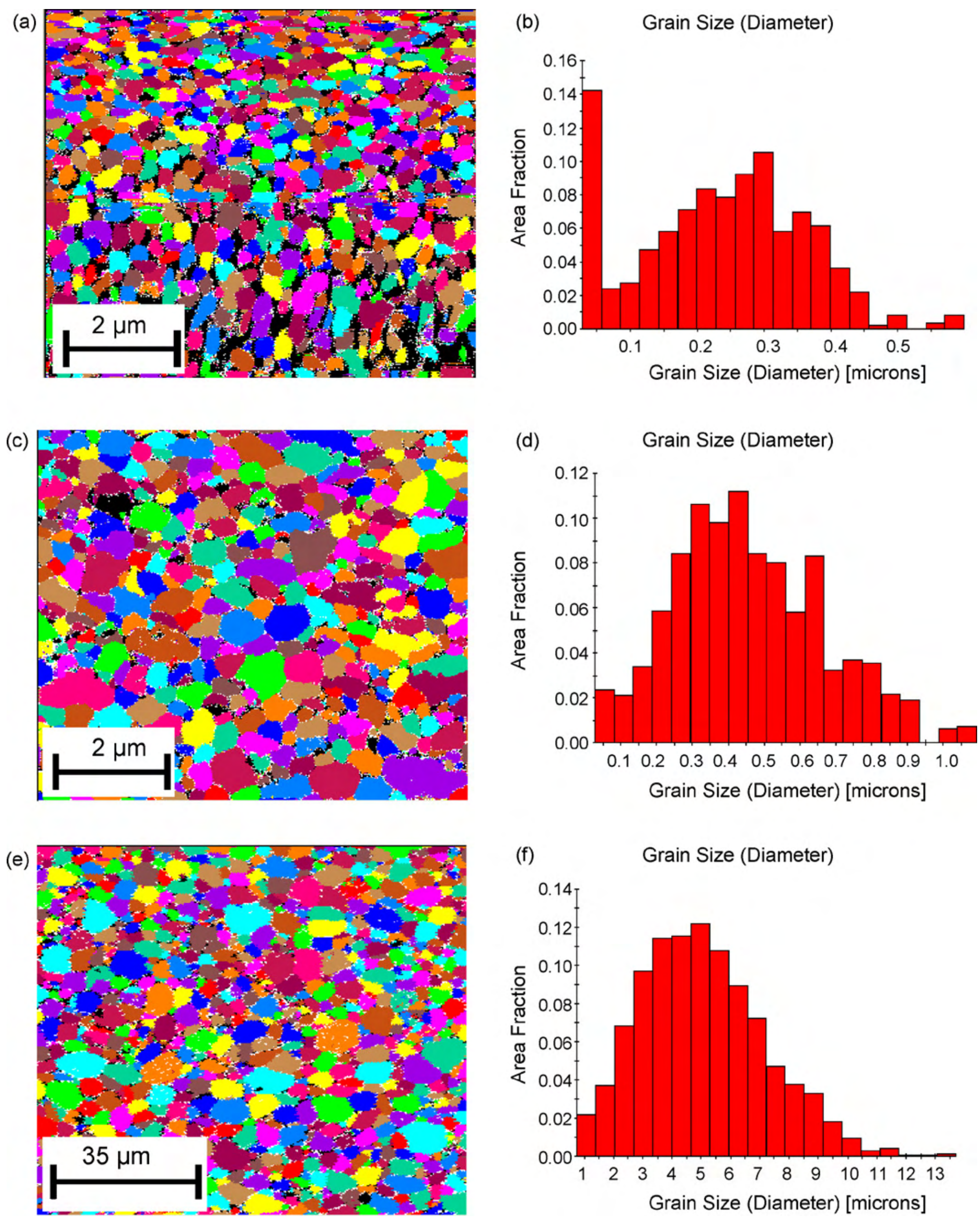

Fig. 6. Orientation map of the measurement area and grain size variation as a function of area fraction of titanium films deposited on silicon at substrate temperature at 200 °C (a and b), at 400 °C (c and d) and 600 °C (e and f). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

influences the observed changes in textures. The thickness of the Ti films was measured by taking cross-sectional view of Ti films by SEM and it was around 6.0 μm of all the samples. Fig. 2 shows the cross-sectional view of Ti film deposited at 200 °C, 400 °C and 600 °C. Atomic force microscopy was used to study the surface topography of Ti films. Fig. 3 shows the AFM images of the Ti samples deposited at substrate temperature ranging from 100 °C to 600 °C, respectively. It can be clearly seen from the images that up to the substrate temperature of 200 °C, the grains are of two-dimensional hexagonal structure and with further increase in the substrate temperature, the grains size increases and it transforms into three-dimensional hexagonal structure. The anisotropic grain growth, thermal stress and texture of the grains are responsible for evolution of three-dimensional hexagonal structures at higher substrate temperature (600 °C). The anisotropic grain growth may occur in Ti thin films due to the factors such as preferred orientation of the grains, orientation-dependent grain boundary mobility and grain boundary free energy, and residual stress.

Fig. 4 shows the SEM images of the Ti films deposited at substrate temperature ranging from 100 °C to 600 °C, respectively. The formations of two- and three-dimensional hexagonal structures of the grains in Ti thin films are evident from this SEM micrograph. Fig. 5 shows the 60° tilted SEM images of Ti films deposited at substrate temperature 600 °C and these images were taken at two different acceleration voltages, i.e. 3 kV and 20 kV. At 3 kV due to the less signal, the image gives different shades that confirms the three-dimensional hexagonal structure. The shades have disappeared when the acceleration voltage increased up to 20 kV.

EBSD has been used to obtain the grain size distribution of the Ti thin films deposited at substrate temperature ranging from 100 °C to 600 °C. To obtain best EBSD patterns, the imaging conditions in the FE-SEM were optimized through tilting the sample and adjusting the working distance so that the higher interaction volume was realized. For EBSD measurement, areas of 12 μm × 12 μm was selected and approximately 450,000 measurement points were collected in a file for the analysis. The surface map of Ti in Fig. 6(a) shows the orientation of the grains in the chosen area of the sample. The orientation of each grain is described by the three Euler angles and characterized by a distinct color. The values of the Euler angles are coded by different intensities of the fundamental colors red, green and blue. The superposition of these components results in the color associated with the orientation of the grain [18]. The EBSD results of Ti thin films showed the increase in grain size with increase in deposition temperature and they are in tandem with that of the analyses made by XRD and AFM. The average grain size by EBSD is 0.235 μm, 0.461 μm and 3.475 μm at 200 °C, 400 °C and 600 °C, respectively. Fig. 6(b, d and f) shows the grain size variation as a function of area fraction at substrate temperature 200 °C, 400 °C and 600 °C, respectively. The uniform grain size distribution is observed for the films grown at 200 °C and 400 °C. The increase in grain size is due to higher driving force associated with grain boundary free energy of the films formed at higher substrate temperature. The grain growth of Ti thin films occurs due to the enhanced mobility of adatoms in the grain boundaries at higher temperature. The grain size distribution of Ti films at higher substrate temperature (600 °C) observed in the present work is not uniform due to the anisotropic grain growth of the thin films, which is influenced by texture of the grains. According to Thompson [19], abnormal grain growth in thin films can occur when the growth of subpopulation of grains (preferred grains) is favoured due to the minimization of surface and interface energy or strain energy minimization. However, the anisotropic grain growth is not pronounced in the thin films up to the substrate temperature of 200 °C.

4. Conclusion

The morphological characteristics of Titanium films deposited on Si (1 0 0) substrates at different substrate temperatures were investigated in the present work. The Ti film showed a (0 0 2) preferred orientation and its intensity increases with increase in the substrate temperature around 200 °C. At above 300 °C, the (1 0 1) preferred orientation has increased while (0 0 2) orientation decreased. The FE-SEM analysis of the Ti films, deposited in Ar atmosphere revealed two- and three-dimensional hexagonal structure of grains depending upon the deposition temperature. The increase in grain size of Ti thin films with increasing deposition temperature was confirmed by XRD, FE-SEM/EBSD and AFM. The grain size distribution is uniform for the films deposited at 200 °C and 400 °C but it transforms into non-uniform distribution for the films deposited at 600 °C. The anisotropic grain growth observed at higher substrate temperature is due to the texture of the grains.

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