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Morphological study of RF magnetron sputtered silicon thin films on AISI 304 stainless steel

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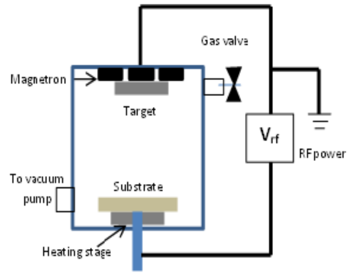
Graphical abstract



Abstract

Silicon thin films on AISI 304 stainless steel were deposited using RF magnetron sputtering. The effect of substrate temperature on the film properties were investigated as the films were prepared at different substrate temperature. Solid phase reaction between Si and Fe from the substrate has led to the formation of single crystal hexagonal shape Fe_2Si layer on the surface of 304 stainless steel (cubic crystal). Film morphology characterized by field emission scanning electron microscope (FE-SEM) and atomic force microscope (AFM) showed the films acquired zone T microstructure and surface roughness was increased with temperature. The film adhesion strength was determined according to VDI 3198 standard for Rockwell-C indentation test. Results from indentation showed good films adhesion was formed and no extended delamination of the films was observed.

Keywords: Si thin film; AISI 304 stainless steel; sputtering; diamond deposition

■1.0 INTRODUCTION

In coating engineering, silicon has been used widely as an intermediate layer between diamond coating and stainless steel because direct diamond deposition poses many problems which difficult to overcome. These problems including carbon diffusivity into iron forming cementite phase (Fe_3C) instead of diamond nucleation, graphitization due to catalytic effect of iron (Fe) on growth and stabilization of sp^2 dominated amorphous black carbon (graphite) and also the large mismatch of thermal expansion co-efficient between diamond and stainless steel usually will cause poor adhesion and high residual stress[1-3]. To overcome these problems, one of the ideas is by introducing an interlayer between diamond coating and steel substrate. This interlayer shall be able to prevent carbon-iron diffusion during diamond deposition. In this work, silicon has been chosen because Si has its own unique advantages over other materials when deposited on stainless steel as interlayer. The properties of silicon coating on stainless steel can be improved by developing silicon intermetallic compounds, the iron silicides; that is, alloying silicon with iron (Fe) during thin film fabrication (either using iron silicide target or by promoting Fe-Si diffusion by increase deposition temperature)[4-5]. By forming iron silicide, the properties of silicon coating such as ductility, toughness and oxidation resistance were improved significantly. Furthermore, silicon carbide (SiC) layer which expected to form during the early stages of CVD diamond deposition on Si has similar crystal structure to diamond, therefore the nucleation kinetics and film adhesion of diamond on the interlayer are expected to be good. Si thin films have been deposited on stainless steel using Ion Beam Deposition (IBD) and CVD as reported by Alvarez et.al[2] while in present work, we choose to deposit Si using RF magnetron sputtering because this process has higher deposition rate than IBD and also can be operated at much lower temperature than CVD process in order to avoid structure changes in stainless steel substrate. However to produce good Si films, the influence of various process parameters such as substrate temperature, pressure and RF power on the morphological behavior are need to be thoroughly studied. This paper shall contribute information regarding to the effect of substrate temperature on the structure, morphology, crystallinity and adhesion properties of the Si films on stainless steel substrate at substrate temperatures of 300°C and 350°C.

■2.0 EXPERIMENTAL

2.1 Deposition of Si films

Silicon was deposited by RF magnetron sputtering on mirror –polished AISI 304 stainless steel substrate (3mm thick) from a 99.99% pure Si target (3-inch diameter and 0.25-inch thick). Substrates were cleaned by rinsing in ultrasonic baths of deionized water and dried under nitrogen gas. The sputtering was carried out in argon (Ar) atmosphere. The ambient (Ar) gas pressure and flow rate was kept at 10mTorr and 30sccm respectively. Before deposition, the chamber was evacuated greater than 10^{-5} torr. The target-substrate distance was 140 mm. The Si films were deposited at RF power of 200 W and the substrate was heated-up to 300^{o}C to promote diffusion. The deposition time was 60 min and the substrate plate was rotated at 10rpm for uniform deposition. The deposition was repeated with substrate temperature of 350^{o}C, while other parameters remain constant.

2.2 Characterization

After depositions, films microstructure and chemical compositions were analyzed using FESEM-Energy dispersive X-ray (EDX) (SUPRA 35-VP) at acceleration voltage of 10 kV. Texture analysis and phase identification were made by X-ray diffraction using Cu Kα radiation 1.5406 Å with scan range from 20^{o} – 100^{o} (2-Theta). Surface morphology of the films was studied using AFM operated in semi-contact (tapping) mode. The study of films adhesion on substrate was conducted according to VDI 3198/1991 (indentation test evaluation of a reliable qualitative control for layered compounds) using maximum load of 150 kg.

■3.0 RESULTS AND DISCUSSION

3.1 FE-SEM

The micrograph in Figure 1 shows the cross-sectional view of the thin film. The layers are homogenously formed with nearly 400 nm thick for both substrate temperatures. This type of microstructure is matching to microstructure of Zone T (Transitional zone) according to structural zone model suggested by Thornton[6] as shown in Figure 2. Based on sputtering parameters (argon pressure and substrate temperature) this model has been accurately predicting the microstructure of our deposited Si film. Microstructure image of film's surface are shown in Figure 3. The FESEM image shows films with very fine grains which producing uniform and smooth surface.

3.2 EDX

Higher substrate temperature has significantly increased the Fe element concentration in the films. From EDX chemical mapping (Table 1), the at% of Fe increases as much as 11% after the substrate temperature was increased from 300^{o}C to 350^{o}C. The quantification result of EDX in Table 1 indicates that the concentration ratio of Fe and Si as 2:1 and 3:1 for each temperatures, respectively. Further substrate heating higher than 350^{o}C shall result the formation of Fe_3Si phase until the depletion of Si. Based on this observation, it is not recommended to deposit 300-400 nm thick Si film on stainless steel with substrate heating exceeding 350^{0}C which to be used as diamond interlayer because the fact that the quality of the diamond films is depending on the saturation of the Si on surface has already been highlighted by few past studies including Singh *et al.*[1] and Alvarez et al[2]. Results from their study have showed that the density of diamond nucleation is correspondingly increased with Si concentration on surface. The main reason is that the saturated silicon will bond with carbon to form stable SiC and allow diamond nucleation on it while inhibit graphitization [2,6,8].

3.3 X-ray Diffraction

Figure 4 (a) and (b) show the profile peaks for films prepared at 300^{o}C and 350^{o}C respectively. The silicide films are identified as Fe_2Si phase (Hexagonal-closed packed) of $(1\ 0\ \bar{1}\ 2)$ and $(1\ 1\ \bar{1}\ 0)$ texture orientation. Based on intensity difference, we conclude that the Fe_2Si films have grown with strong preferred orientation of $(1\ 0\ \bar{1}\ 2)$ direction as the intensity of $(1\ 1\ \bar{1}\ 0)$ direction is very low. Meanwhile, no Si peak is found and we presumed that all Si has reacted with Fe to form iron silicide, Fe_2Si phase. By increasing in substrate temperature (+50^{o}C) it has resulting small intensity changes on the Fe_2Si preferred orientation.

Table 1 Fe-Si concentration ratio obtained by FE-SEM EDX for different substrate temperatures

	300^{o}C	**350^{o}C**
Element	Atomic %	Atomic %
Si K	35.24	23.96
Fe K	64.76	76.05

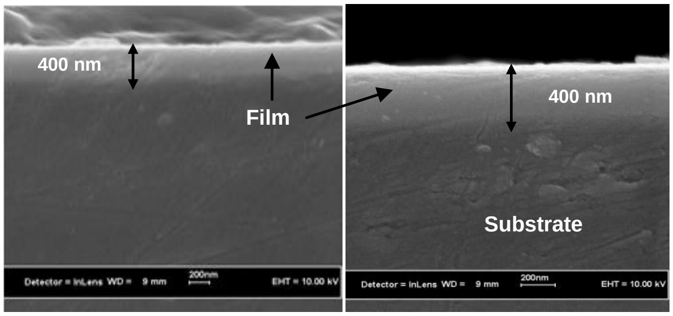


Figure 1 Cross-sectional view of silicide thin films on AISI 304 stainless steel deposited at substrate temperature of 300^{o}C (Left) and 350^{o}C (Right)

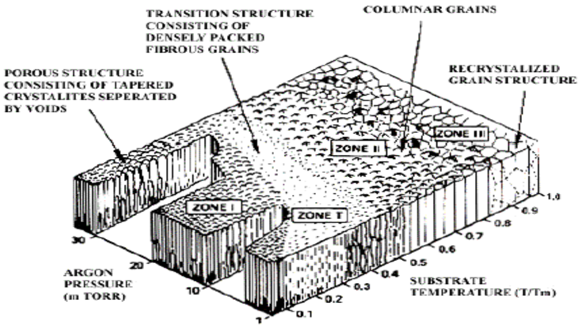


Figure 2 Thornton structure zone model (SZM)[9]

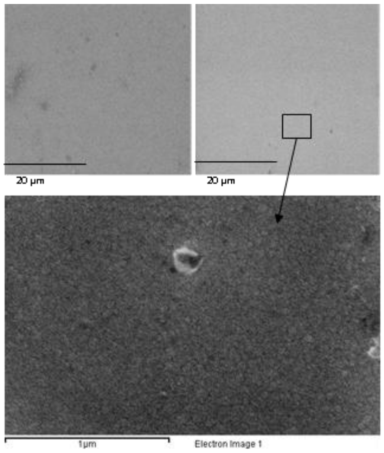
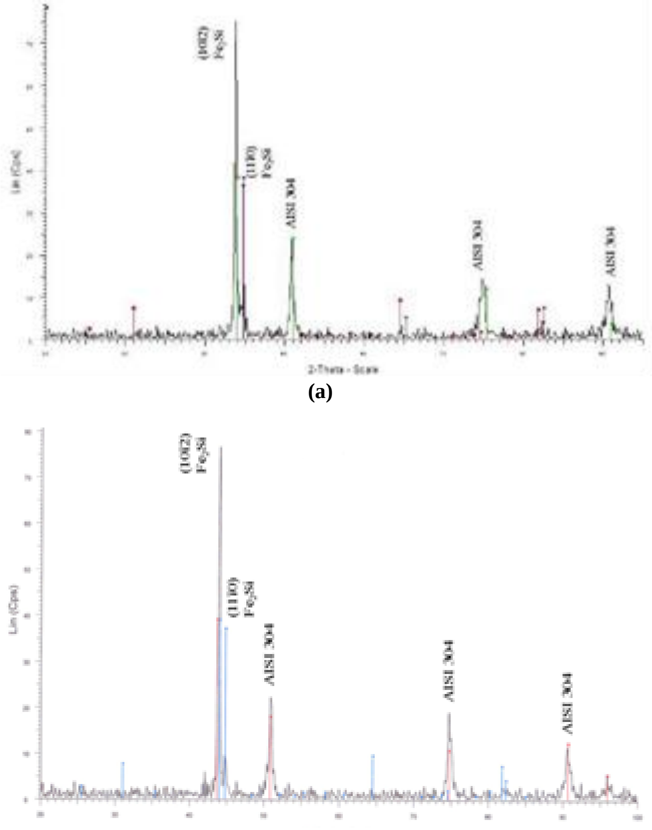


Figure 3 FE-SEM surface image of silicide thin films on AISI 304 stainless steel deposited at substrate temperature of 300^{o}C (Top left) and

350°C (Top right). The image in the small box is magnified as shown in bottom image



(a)

(b)

Figure 4 XRD profiles for Si films deposited at substrate temperature of (a) 300°C and (b) 350°C

3.4 AFM

The 4µm x 4µm AFM topographs of Fe_2Si films in Figure 5 (a) and (b) have revealed differences in surface morphology when the films were prepared at different substrate temperature. The different features can be seen on surface roughness and grain size, it is pronounced that larger grained are observed on sample deposited at 350°C which result in higher surface roughness value. Higher temperature results in higher adatoms mobility and surface diffusion which promote grain growth. The influence of temperature and surface diffusion on grain growth of nanocrystalline thin film is described in equation (1). Where D is the mean grain diameter after some time t (cm^2/s), D_0 is the initial grain diameter, K_0 is a constant (cm^2/s), Q is the activation energy (J/mol) for the process, R is gas constant (J/mol.K) and T is temperature (K).

$$(D^2 - D_0^2)/t = K_0 e^{-Q/RT} \qquad (3.1)^{10}$$

Some abnormal grain growth occurred on films deposited at both temperatures of 300°C and 350°C as shown in (Figure 5 (c) and (d)). Abnormal grain growth may occur when the coarsening of some grains is suppressed or augmented by a variety of effects including film strain, impurities and shadowing effects [11-13].

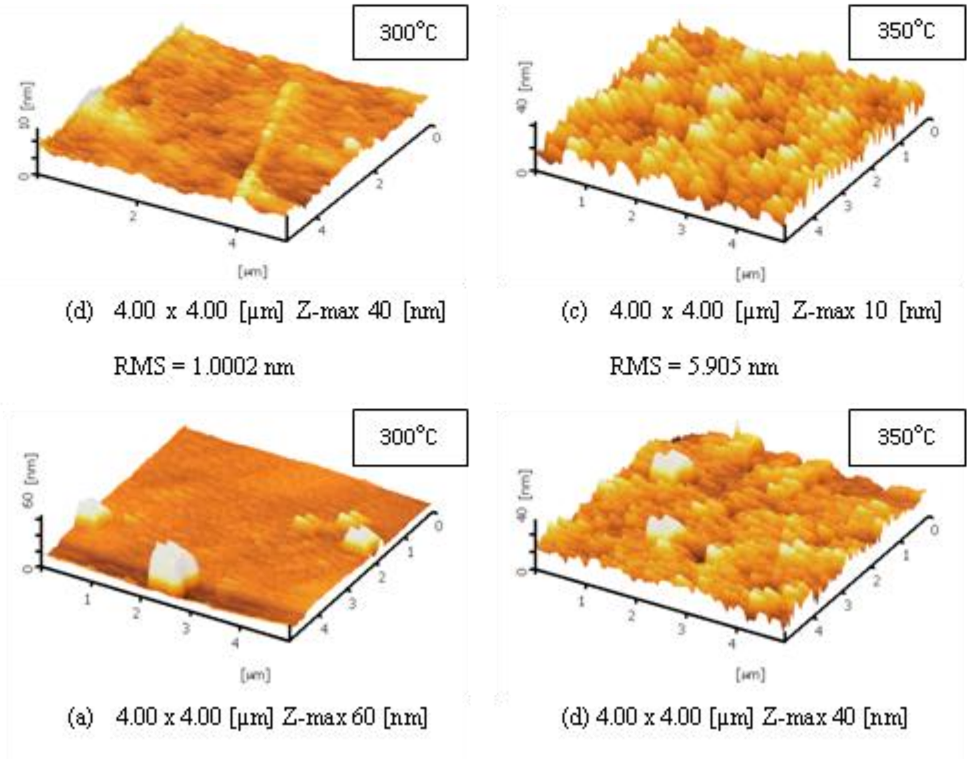


Figure 5 AFM 3D image for iron silicide films deposited on AISI 304 SS. (a) Film deposited at 300oC, (b) Film deposited at 250oC, (c) Abnormal grains at 300oC and (d) Abnormal grains at 350oC

3.5 Indentation Test

The test is conducted according to VDI 3198/1991 (indentation test evaluation of a reliable qualitative control for layered compounds)[14] to test film's adhesion on substrate. This destructive test is based on Rockwell C indentation test on planar surfaces or coated compounds. The adhesion strength is classified as HF 1 to HF 4 for sufficient adhesion and HF 5 to HF 6 for insufficient adhesion (refer to Figure 6). The term "HF" was the short form for adhesion strength. The indentation was used 150 Kg impact load on coated surface and cause layer damage adjacent to the boundary of the indentation.

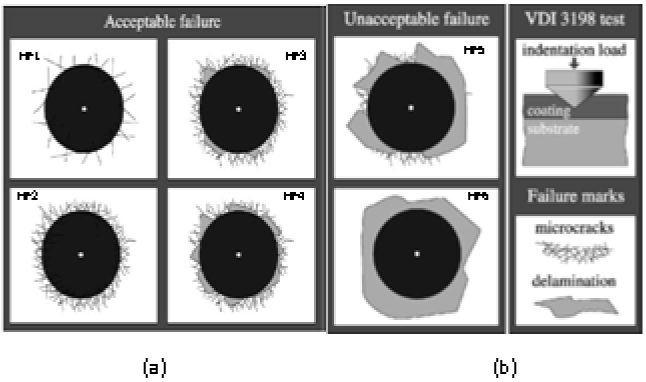


Figure 6 (a) Four different textures above used as indication to determine film adhesion on its substrate [14]. HF1 (good adhesion) – HF4 (sufficient adhesion) (b) HF5 and HF6 types of failure indicate very poor surface adhesion [14]

Figure 7 shows the types of failure mark on Fe_2Si films after indentation. Both films prepared at different substrate temperatures show small delamination area and circular bulge wrinkles adjacent to the indentation crater. However, no extended delamination or chipping of the film was found. The adhesion of iron silicide films formed at 300°C and 350°C can be categorized as HF3 "Acceptable failure."

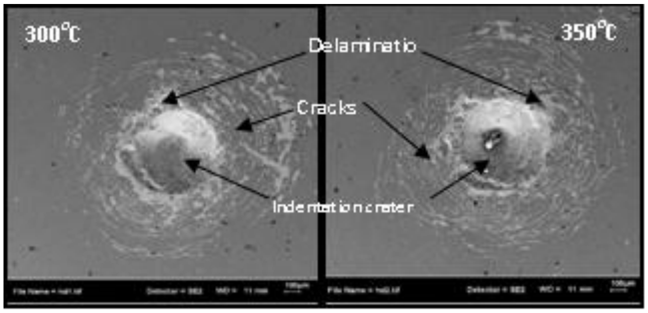


Figure 7 FESEM images of indented films of different deposition substrate temperature (left) 300°C and (right) 350°C

■4.0 CONCLUSION

400 nm thick Si films were deposited using rf magnetron sputtering on AISI 304 stainless steel which to be functioned as interlayer for diamond coating. The effects on films properties after grown with substrate temperatures of 300°C and 350°C were investigated in this work and have been summarized as followed.

1. Films deposited at substrate temperatures of 300°C and 350°C (0.2, 0.25 T/T_m) are having zone T microstructure according to Thornton structure zone model.
2. EDX analysis described Fe concentration in films increase to 11% for 50°C increases of substrate temperature.
3. From XRD analysis single crystal $(1\ 0\ \bar{1}\ 2)$ orientation HCP Fe_2Si films have formed but no crystalline of pure Si detected in thin films probably due to low degree of crystallinity (a:Si). There is increment in degree of crystallinity of preferred orientation with increasing in temperature.
4. Grain size and surface roughness increases with temperature.
5. Films deposited at substrate temperature of 300°C and 350°C demonstrates good adhesion on austenitic stainless steel substrate.

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