Effects of Substrate Temperature on Ti-Si-C Thin Film Deposited by Sputtering Using Elemental Targets

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Abstract. Deposition of Ti-Si-C thin films by magnetron sputtering was examined using elemental targets of titanium, silicon and carbon, in order to investigate the effects of substrate temperature on the formation of carbide compounds such as TiCₓ and/or Ti₃SiC₂, and thereby on mechanical properties and on physical properties of the thin films. It was found that Ti-Si-C thin films of both excellent electrical conductivity and high hardness could be formed by depositing at much lower temperature than the conventional depositing temperature such as 800 degree centigrade. And it was noteworthy that the Ti-Si-C film of electrical resistivity around 200 μΩcm and hardness higher than 10GPa could be obtained by depositing at 500 degree centigrade.

1. Introduction
Ternary carbide compounds known as Mₙ₊₁AXₙ phases (M: early transition metal, A: A-group elements, X: C and/or N, n=1~3) have not only the benefits of ceramics such as resistance against oxidation and a high decomposition temperature but also metallic properties like ductility, electrical and thermal conductivity [1,2]. Thin films consisting of the MAX-phase family, in particular Ti₃SiC₂ phase, can be highly expected to be applied for electrical contacts, etc., thanks to their own good electrical conductivity. However the formation of Ti₃SiC₂ phase is competitive with the growth of TiCₓ phase through Si segregations or Si substitutional incorporations in TiCₓ [3]. Moreover thin films within the MAX phase can only be synthesized at preparation temperatures above 700 degrees centigrade and on textured or single crystalline substrates [4].

Nevertheless lower preparation temperatures are more practical in applying the thin films for protective coatings of not only metallic conductivity but also excellent resistance against wear and/or corrosion. Therefore the deposition of Ti-Si-C thin films by magnetron sputtering was examined using elemental targets of titanium, silicon and carbon, in order to investigate the effects of substrate temperature on the formation of carbide compounds such as TiCₓ and/or Ti₃SiC₂, and thereby on mechanical properties such as hardness and on physical properties such as electrical conductivity of the thin films.

2. Experimental procedure
A planar magnetron sputtering system (ANELVA L-332S-FHS) with three cathodes was used. The planar targets used for the sputter-deposition of Ti-Si-C thin films were a pure titanium disk, a pure silicon disk, and a pure carbon disk of 80 mm diameter. Si(100) substrates (12x10mm², thickness 0.35mm) were mounted on the substrate holder at room temperature, and heated at 500 or 800 degree
The thin films were deposited on the substrates in an atmosphere of argon at a pressure of 0.4 Pa by co-sputtering of the three elemental targets with an RF electric power supply and two DC electric supplies respectively, where an independent electric power source was used for the sputtering of each target. The two DC power supplies for sputtering the titanium target and carbon one were respectively fixed at DC120W and DC150W, while the RF power supplied for sputtering the silicon target was fixed at RF50W. The deposition time was of 40min, and the substrate holder was rotated with 20r.p.m. during the sputter-deposition to obtain uniform deposition conditions for homogeneous film composition over the substrate area. The schematic illustration of the co-sputtering system for the deposition of Ti-Si-C thin films is shown in Fig.1.

Characterization of the obtained films was performed by X-ray diffractometry (XRD). And the electrical resistivity of the films was measured by the four-point-probe method. A resistivity correction factor (RCF) of 4.532 was used to calculate the resistivity. Furthermore the indentation hardness was measured using a dynamic ultra-microhardness tester (Shimadzu DUH-201S) with a Vickers indenter. Uploading tests following loading tests were performed to exclude the displacement caused by elastic deformation. Thus, the dynamic hardness was calculated from the depth of indentation as a result of plastic deformation.

Figure 1. Schematic illustration of the co-sputtering system for the deposition of Ti-Si-C thin films onto Si(100) substrates.

3. Results and Discussion

3.1. Structural properties

The obtained Ti-Si-C thin films appeared to be uniform and adhesive, and they appeared metallic and dark gray. Figure 2 shows the X-ray diffraction patterns of the Ti-Si-C thin films deposited at room temperature, at 500 and 800 degree centigrade. It should be noted that in the figure the intensity obtained for the 500 degree centigrade is shifted by +200 cps while that for the 800 degree centigrade is shifted by +400 cps. The diffraction pattern of the film obtained at 800 degree centigrade exhibited peaks for a titanium carbide phase of TiC and a titanium silicide phase of Ti$_5$Si$_3$ as well as a MAX phase of Ti$_3$SiC$_2$. Thus it was found that the MAX phase (Ti$_3$SiC$_2$), the carbide phase (TiC) and the silicide phase (Ti$_5$Si$_3$) were formed in the Ti-Si-C film. On the other hand, any distinct diffraction peaks were not detected but a halo pattern was detected for the film obtained at 500 degree centigrade and a broad peak was detected for the film obtained at room temperature. Upon more detailed observation of the broad peak, it was guessed that the peak contained the diffraction by Ti(002) plane because of its peak-position. Thus it was assumed that fine crystals of α-titanium existed in the Ti-Si-C film. On the other hand, it was guessed that the halo pattern obtained at 500 degree centigrade...
reflected the formation of those MAX, carbide and silicide phase because of its pattern and its peak-position. Thus it was assumed that fine crystals of the MAX, the carbide and/or the silicide phase might also exist in the Ti-Si-C film, but which is not still clarified from the result of the XRD.

Figure 2. X-ray diffraction patterns of the Ti-Si-C thin films deposited onto Si(100) substrates, which were obtained at room temperature, 500°C and 800°C.
3.2. Electrical resistivity
Figure 3 shows the electrical resistivity of the Ti-Si-C thin films deposited at room temperature, at 500 and 800 degree centigrade. The electrical resistivity of the thin film obtained at 800 degree centigrade was of around 160 μΩcm, while the others were of around 220 μΩcm, finding that they had excellent electrical conductivity, compared with the electrical resistivity (approximately 3000 μΩcm) of chromium oxycarbide films having similar physical and chemical properties.[5] Then the electrical conductivity of the films obtained at 500 degree and 800 degree centigrade seemed to be due to the formation of the MAX phase (Ti$_3$SiC$_2$) and/or the carbide phase (TiC) while that obtained at room temperature seemed to be due to the formation of the α-titanium phase, considering the above-mentioned results of XRD.

![Graph showing electrical resistivity](image)

**Figure 3.** Electrical resistivity of of the Ti-Si-C thin films deposited onto Si(100) substrates, which were obtained at room temperature, 500°C and 800°C.

3.3. Surface hardness
The displacement of the indenter in the loading process was caused by both elastic and plastic deformation. On the other hand, the displacement in the unloading process was caused by elastic deformation. Thus, the dynamic hardness was calculated from the displacement of the indenter caused by only plastic deformation, excluding that caused by elastic deformation.

Figure 4 shows the dynamic hardness of the Ti-Si-C thin films deposited at room temperature, at 500 degree and 800 degree centigrade normalized by that of a Si(100) wafer whose hardness is approximately 10GPa. The hardness of the film obtained at 500 degree centigrade was the highest of those under the three conditions, and the hardness was estimated to be approximately 11GPa by comparing with that of Si(100) substrates. Then the high surface hardness seemed to be due to the formation of the binary carbide TiC phase while the lower surface hardness of the film obtained at room temperature and at 800 degree centigrade seemed to be respectively due to the formation of the α-titanium phase and that of the MAX phase (Ti$_3$SiC$_2$), because the Vickers hardness of ultrafine-grained titanium phase has been reported to be approximately 4 Gpa [6], and because the ternary carbide Ti$_3$SiC$_2$ is relatively soft and its Vickers hardness has also been reported to be approximately 4GPa. [7,8]
4. Conclusions

Based on XRD, it was found that a titanium silicide phase of Ti₅Si₃ as well as titanium carbide phases such as Ti₃SiC₂ and TiC were formed in the film obtained at 800 degree centigrade. On the other hand, any distinct diffraction peaks were not detected, but a halo pattern was detected for the film obtained at 500 degree centigrade and a broad peak was detected for the film obtained at room temperature. Then, because of those pattern and those peak-position, it was assumed that fine crystals of α-titanium existed in the Ti-Si-C film obtained at room temperature while fine crystals of the MAX, the carbide and/or the silicide phase might also exist in the Ti-Si-C film obtained at 500 degree centigrade. The electrical resistivity of the thin film obtained at 800 degree centigrade was of around 160μΩcm, while the others were of around 220μΩcm, finding that they had excellent electrical conductivity. According to nano-indentation tests, the hardness of the film obtained at 500 degree centigrade was the highest of those under the three conditions, and was estimated to be approximately 11GPa by comparing with that of Si(100) substrates.

Therefore it was found that Ti-Si-C thin films of both excellent electrical conductivity of around 200 μΩcm and surface hardness higher than 10GPa could be formed by depositing at much lower temperature of 500 degree centigrade than the conventional depositing temperature such as 800 degree centigrade. Thus it is expected that this deposition process will be more useful for providing protective coatings for electrical friction contacts.

References

[1] K. L. Choy and E. Felix, Mater. Sci. Eng. A278, 481 (2000)
[2] J. Emmerlich, H. Hoegberg, S. Sasvari, P. O. A. Persson and L. Hultman, J. Appl. Phys. 96, 4817 (2004)
[3] A. A. Woevodim and J. S. Zabinski, Diamond Relat. Mater. 7, 463 (1998)
[4] C. Lopes, N.M.G., Parreira, S. Carvalho, A. Cavaleiro, J.P. Riviere, E. Le Bourhis and F. Vaz, Surf. Coat. Tech. 201, 7180 (2007)
[5] T. Kado, Y. Noda, Jpn. J. Appl. Phys. 28, 1450 (1989).
[6] K. Edalati, Z. Horita, Scripta Materialia 64, 161 (2011)
[7] T. El-Raghy, M. W. Barsoum, A. Zavaliangos and S. R. Kalidindi, J. Am. Ceram. Soc. 82, 2855 (1999).
[8] M. Radovic, M. W. Barsoum, T. El-Raghy, J. Seidensticker, and S. Wiederhorn Acta Mater. 48, 453 (2000)