Extended Abstracts of the 2013 International Conference on Solid State Devices and Materials, Fukuoka, 2013, pp288-289

Synthesis of MAX-Phase Containing Ti-Si-C Films by Sputter-Deposition Using Elemental Targets

Tsutomu Sonoda, Setsuo Nakao and Masami Ikeyama

National Institute of Advanced Industrial Science and Technology (AIST)
2266-98 Anagahora Shimoshidami, Moriyama-ku, Nagoya 463-8560, Japan
Phone: +81-52-736-7480 E-mail: tsutomu.sonoda@aist.go.jp

Abstract

The synthesis 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 carbon contents in the films on the formation of such carbide compounds as TiC and/or Ti_3SiC_2. The thin films were deposited on silicon substrates heated at around 800 degree centigrade in the atmosphere of argon. Obtained Ti-Si-C films were composite materials consisting of Ti_3SiC_2 MAX phase, TiC phase and graphite phase. Physical and mechanical properties of the film depended on each amount of these 3 phases. And the each amount of these 3 phases depended on the carbon content in the film. Thus film properties could be controlled by the amount of carbon supplied by sputter-deposition. A noteworthy electrical resistivity less than 80μΩcm was achieved.

1. Introduction

Ternary carbide compounds known as $M_{n+1}AX_n$ 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]. Thin films consisting of the MAX-phase family, in particular Ti_3SiC_2 phase, can be highly expected to be applied for electrical contacts, etc., thanks to their own good electrical conductivity [2]. However the formation of Ti_3SiC_2 phase is competitive with the growth of TiC phase through Si segregations or Si substitutional incorporations in TiC.

Moreover the scientific information on the formation of the MAX-phase is very important in applying the Ti-Si-C thin films containing the MAX-phase for electronic components such as electrical friction contacts because electrical contacts require high wear resistance and good electrical conductivity as well as good thermal stability at the processing temperature.

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 carbon contents in the films on the formation of ternary carbide compounds such as Ti_3SiC_2, and thereby on physical properties such as electrical conductivity or mechanical properties such as hardness.

2. Experimental

A planar magnetron sputtering system (ANELVA Corp. type L-332S-FHS) with 3 cathodes was used. The planar targets used for sputter-deposition of Ti-Si-C thin films were a pure titanium disk, a pure silicon one and a pure carbon one of 80 mm in diameter. Si(100) substrates ($12\times10mm^2$, thickness 0.35mm) were mounted on the substrate holder heated at around 800 degree Celsius. The thin films were deposited on the substrates in the atmosphere of argon at the pressure of 0.4Pa by co-sputtering of three elemental targets, where three independent electric power sources were used for sputtering each target. Sputtering conditions were as follows. The DC power and the RF power supplied for sputtering the titanium target and the silicon one were respectively fixed at DC120W and RF50W, while the DC power supplied for sputtering the carbon target was varied with the step of 100W step from 400W to 200W to vary the carbon content in the deposited films. Each depositing time was adjusted so that its film thickness might be the same as around 300nm thick. Thereby the time ranged from 30 min to 37 min. During the sputter-deposition, the substrates were rotated with 20 r.p.m. to obtain uniform deposition conditions for homogeneous film composition over the substrate area.

3. Results and Discussion

Structural properties

Obtained Ti-Si-C films appeared to be uniform and adhesive, and they looked metallic and dark grey. The chemical composition of the Ti-Si-C films changed with the sputtering conditions, i.e., Ti, Si and C contents were about 39, 9 and 52 at.% , about 44, 12 and 44 at.% , and about 50, 15 and 35 at.% for the films deposited with DC power of 400W, 300W and 200W supplied for sputtering the carbon target, respectively. Figure 1 shows the X-ray diffraction patterns of the Ti-Si-C thin films deposited with DC power of 200W, 300W and 400W supplied for sputtering the carbon target. Every diffraction pattern showed peaks for the TiC phase, some of which were broad or indistinct. Thus the formation

of the carbide TiC was found in every Ti-Si-C thin film. On the other hand, the diffraction pattern of the film obtained with DC power of 200W also showed peaks for the Ti_3SiC_2 phase. Thus the formation of the ternary carbide of MAX-phase Ti_3SiC_2 was also found in the Ti-Si-C film deposited with DC power of 200W. Therefore it was found that the Ti_3SiC_2 phase as well as TiC phase were formed in the film obtained under an electric power of DC200W while TiC phase predominantly formed under an electric power higher than DC300W.

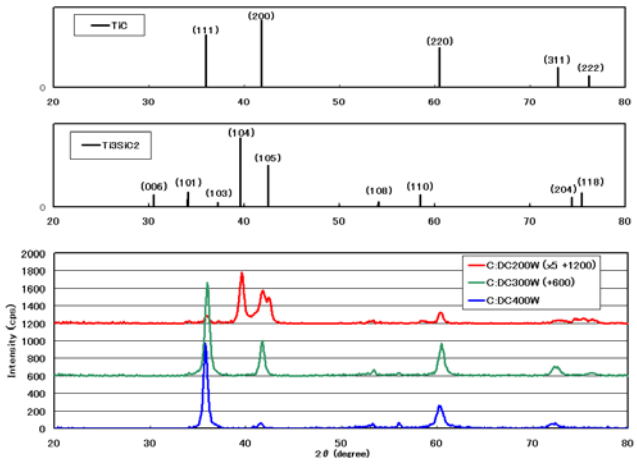

Fig. 1 X-ray diffraction patterns of Ti-Si-C films deposited with DC powers of 200, 300 and 400W supplied for the carbon target.

Microstructure

According to M. Amer, et al. and M. Rester et al., Raman spectrum of the ternary carbide Ti_3SiC_2 has specific sharp peaks at 159, 228, 281, 312, 631 and 678cm^{-1}, while that of the carbide TiC has wide peaks around 265, 340, 372, 596, 661cm^{-1} and so on [3,4]. The Raman spectrum of the film obtained under an electric power of DC200W for the carbon target showed several peaks between 200 and 700cm^{-1}. Thus it was assumed that peaks detected around 631 and 678cm^{-1} were attributed to the ternary carbide Ti_3SiC_2 while peaks detected around 265 and 596cm^{-1} were attributed to the carbide TiC. And the Raman spectrum of the film obtained under the DC300W also showed several peaks between 500 and 700cm^{-1}. Thus it was assumed that peaks detected around 631cm^{-1} was attributed to the ternary carbide Ti_3SiC_2 while peaks detected around 596 and 661cm^{-1} were attributed to the carbide TiC. Furthermore the Raman spectrum of the film obtained under the DC400W showed not only a wide peak between 500 and 700cm^{-1} but also two specific peaks between 1100 and 1700cm^{-1}. Thus it was assumed that the peak detected around 596cm^{-1} was attributed to the carbide TiC_x while the peaks detected around 1360 and 1580 cm^{-1} were attributed to fine graphite crystallites considering the result of X-ray diffraction. Therefore it was found that excess carbon atoms precipitated out as fine graphite crystallites in the Ti-Si-C film.

Electrical conductivity

The electrical resistivity of obtained films decreased with the decrease of the electric power supplied to the carbon target, and that of the film obtained under DC200W was the lowest of those under the three conditions. The minimum electrical resistivity lower than 80μΩcm was noteworthy.

Surface hardness

The hardness of the obtained films decreased with the decrease of the electric power supplied to the carbon target, and that of the film obtained under DC200W was the lowest of those under the three conditions. And it was also assumed that the remarkable decrease of surface hardness resulted from the formation of Ti_3SiC_2 phase in the film. Because the ternary carbide is relatively soft and its Vickers hardness was reported to be approximately of 4GPa [5]. Furthermore it was expected that the electrical resistivity and the hardness of the films could be controlled by the electric power supplied for sputtering a carbon target.

4. Conclusions

It was found that the Ti_3SiC_2 phase as well as TiC_x phase were formed in the film obtained under an electric power of DC200W while TiC phase predominantly formed under an electric power higher than DC300W. Thus it was found that the formation of Ti_3SiC_2 phase or TiC phase depended on the carbon content in the Ti-Si-C films, which was could be easily controlled by an electric power supplied for sputtering a carbon target. And it was also found that the electrical resistivity and the hardness of the films depended on the formation of Ti_3SiC_2 phase or TiC phase. These findings are very important in applying the Ti-Si-C thin films for electronic components such as electrical friction contacts, etc. Because the electrical contacts have to bear both a high wear resistance and a good electrical conductivity as well as a good thermal stability at the processing temperature. Base on the results of this study, it was assumed the structure of deposited films can be controlled by changing the electric power supplied during the sputter-deposition so that its surface layer might have high hardness and at the same time its inner layer might have an excellent electrical conductivity. Therefore it is expected that this depositing process can be very useful in providing protective coatings for electrical friction contacts.

References

[1] J. Emmerlich *et al.*, Acta Mater. **55** (2007) 1479.
[2] H. Hoegberg *et al.*, Surf. Coatings Technol. **193** (2005) 6.
[3] M. Amer *et al.*, J. Appl. Phys. **84** (1998) 5817.
[4] M. Rester *et al.*, Mater. Sci. Eng. A **429** (2006) 90.
[5] T. El-Raghy *et al.*, J. Am. Ceram. Soc. **82** (1999) 2855.