Mater. Res. Soc. Symp. Proc. Vol. 976 © 2007 Materials Research Society 0976-EE03-18

Study of the Effects of Si Addition on the Properties of Hard Nanocomposite Thin Films

Jose Luis Endrino[1], Sergio Palacin[2], Alejandro Gutierrez[2], Myriam Aguirre[3], and Franz Schäfers[4]
[1]Plasma Applications Group, Lawrence Berkeley National Laboratory, 1 Cyclotron Rd. Building 53, Berkeley, CA, 94720
[2]Universidad Autonoma de Madrid, Madrid, Spain
[3]Empa-Swiss Federal Lab for Materials Testing and Research, Duebendorf, Switzerland
[4]BESSY GmbH, Berlin, Germany

ABSTRACT

In the present study, hard TiSiN coating compounds with different Si content have been deposited by the magnetron sputtering technique. X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) have been employed to investigate the effects of Si addition on the composition, structure and phase development of the cubic NaCl-type structure. To get some insight on these changes, X-ray absorption spectra have been measured at the Ti and Si K-edges in fluorescence yield mode. The collected data showed that the interaction between Ti and Si was weak and the formation of a-Si_3N_4 can be assumed. Hardness measurements were also consistent with the formation of hard nanocomposite films. A maximum hardness of about 36 GPa was obtained for the sample with 11 at. % Si.

INTRODUCTION

Addition of silicon to TiN coatings can significantly influence their texture, phase formation and grain size. Nanocomposite materials can exhibit high hardness and possess a high resistance to oxidation, which results in a broad range of mechanical applications [1]. The formation of two-phase nanocomposite systems composed of amorphous Si_3N_4 and nanocrystalline metallic nitride phases has been extensively reported in both transition metal nitride and carbide compounds [2-4]. The low solubility of silicon in the lattice of fcc-NaCl structured nitrides has been explained by the higher mixing enthalpy of complex ternary or quaternary nitride compounds when compared to the lower free energy of MeN and a-Si_3N_4 phases [5]. TiSiN coatings have been subject of detailed structural and chemical characterization by a wide number of analytical techniques [6]. This work reports on the local structure and bonds of titanium and silicon in TiSiN thin films by combining x-ray diffraction (XRD) and the x-ray absorption (XAS) techniques.

EXPERIMENTAL DETAILS

TiSiN coatings investigated in this research were deposited using dual pulsed magnetron sputtering from Ti and Si targets in an Ar/N_2 atmosphere. Mirror-polished squared cemented carbide inserts were used as substrates. The thickness of all the coating samples was within 3.5 ± 0.2 μm. A Siemens D500 diffractometer with a CuKα tube and the $\Theta/2\Theta$ mode was used to perform XRD analysis and identify the phases formed. Chemical analysis was performed on a Field Emission SEM (LEO 1550 FEG) equipped with INCA Energy Dispersive Spectroscopy

(EDS). XAS measurements of the Ti and Si K-edges were carried out at the KMC-1 beamline of the BESSY synchrotron facility with double crystal monochromator using a standard chamber equipped with a high-resolution solid-state fluorescence detector. Si (111) and InSb (111) monochromator crystals were used to provide photon energy selection at the Ti-Kedge and Si K-edge spectra, respectively. Hardness measurements were carried out using a Fischerscope H100C depth sensing indentation instrument.

DISCUSSION

Chemical composition of the metallic component for the Ti-Si-N samples is shown in Table I.

Table I: Composition analyzed by EDS-SEM of the deposited samples.

Sample	Ti (at. %)	Si (at. %)
1	100	-
2	97.1	2.9
3	89.3	10.7
4	76.2	23.8

X-ray Diffraction

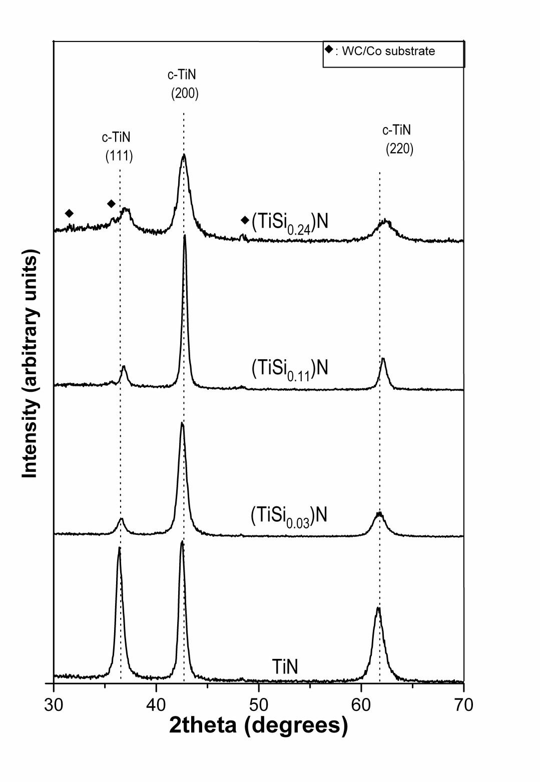

Figure 1. X-ray diffraction patterns.

X-ray diffraction patterns for all the deposited Ti(Si)N films are shown in figure 1. Sample #1 (0 at. % Si) shows a well-defined polycrystalline B1-NaCl microstructure. The peaks coincide with those for B1 structure for titanium nitride (JCPDS Card No. 38-1420). The silicon containing samples also showed a crystalline B1-type structure. In comparison to sample #1, the diffraction patterns of the three deposited silicon-containing samples showed preferred (200) texture. Sample #4 (24 rel. at. % Si) showed amorphous peaks in the (111), (200) and (220) planes but the position of these peaks also appears to be coincidental with the positions marked for the B1-TiN structure.

X-ray Absorption

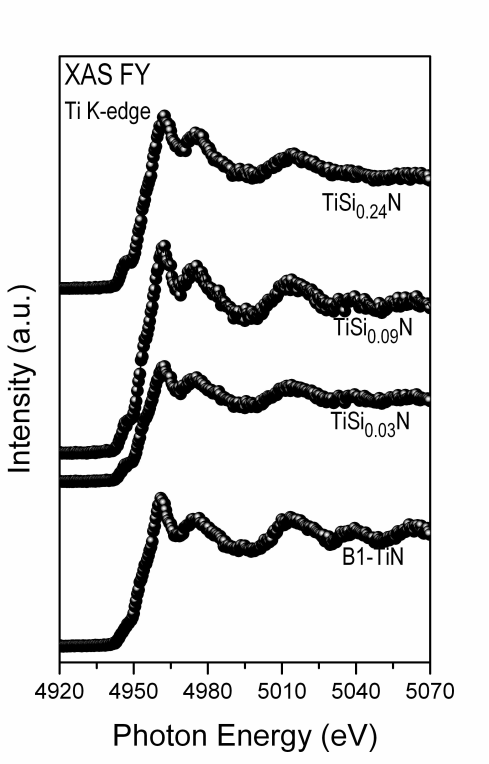

Figure 2. X-ray absorption spectra of Ti K-edge in TiSiN films.

Fig. 2 shows XAS spectra at the Ti K-edge of TiSiN samples with different Si content. In this case, all spectra keep a similar lineshape to that of titanium nitride, independently of Si content. The pre-edge region, which is associated to transitions from Ti-1s states to Ti-3d states hybridized with Si-2p states, does not show significant changes with Si-addition. This suggests a weak interaction between Ti and Si.

Fig. 3 shows XAS spectra at the Si K-edge of TiSiN samples with different Si content, as well as pure Si and SiO_2 single crystals, and an amorphous Si_3N_4 as reference samples for comparison. As can be observed by comparing the top spectrum with all TiSiN spectra, in all cases the spectral lineshape is typical of Si_3N_4. Both features corresponding to Si_3N_4were present in all of the Si-containing samples and there was not any significant change with silicon content.

Hence, both Ti-K and Si-K XAS results suggest that the interaction between Ti and Si is weak and that amorphous Si_3N_4 aggregates are formed inside a TiN matrix.

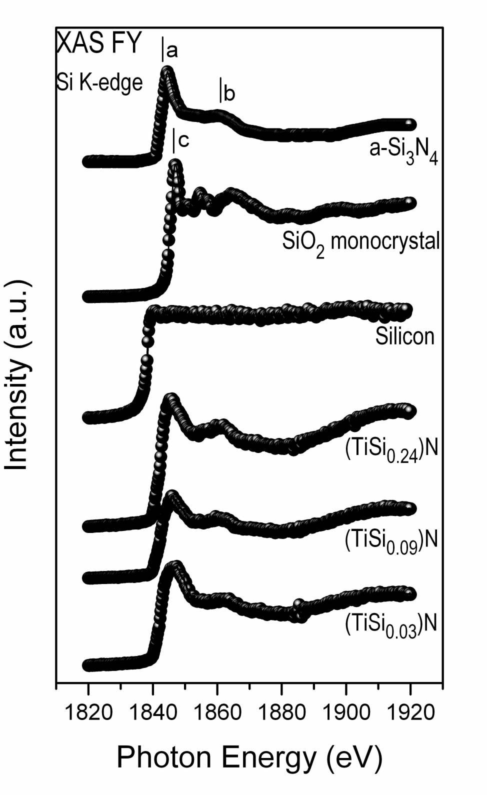

Figure 3. X-ray absorption spectra of Si K-edge for TiSiN films.

Mechanical Properties

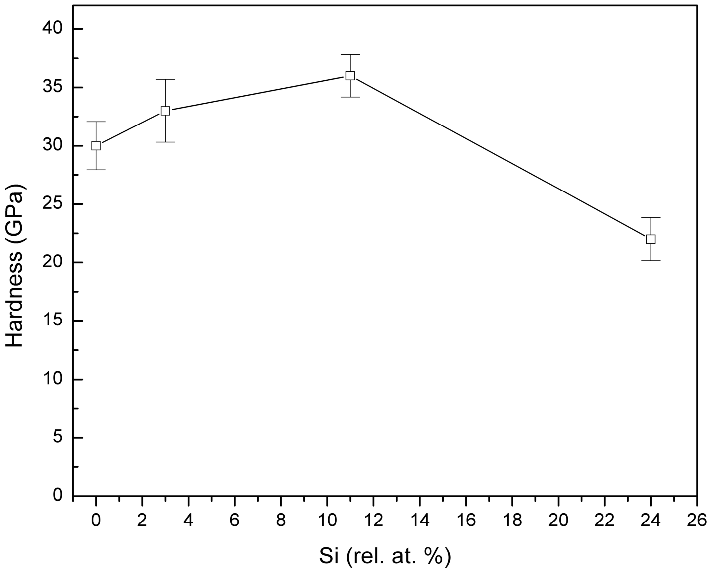

Figure 4. Hardness measurements for deposited films.

Hardness measurements for TiSiN films are shown in figure 4. Two of the silicon containing samples had hardness greater than that of unalloyed TiN. The maximum hardness was achieved by sample #3 (11 rel. at. % of Si), which had an average of ~36 GPa. The hardness increment observed in the two TiSiN compounds with low silicon contents has been in explained the past by the lattice distortion and by dislocation blocking in the TiN nanocrystalline structure [5]. It is reasonable to consider that the hardness drop observed for the sample with high Si content (sample #4) is due to the fact that a-Si3N4 phase percolated through the TiN nanocrystals. Indeed, this correlates well with XAS spectra shown in figures 2 and 3 since there were no significant changes observed in Ti-K and Si-K spectra with silicon addition.

CONCLUSIONS

Thin films within the Ti-Si-N system have been prepared by pulsed magnetron sputtering. X-ray diffraction revealed the formation of just one crystalline B1-TiN phase. Increase in Si content resulted in a change in texture from (111) to (200) and indicated an amorphization of the microstructure. X-ray absorption spectroscopy (XAS) proved to be a very appropriate tool for this kind of study; the collected data also supported the formation of nanocomposite nc-TiN and a-Si_3N_4 phases since there was not any significant change in Ti-K edge and Si K-edge spectra with silicon content. Hardness measurements of the deposited films showed a maximum hardness was achieved by the sample with about eleven atomic percent of silicon.

ACKNOWLEDGMENTS

This work was supported by the EU - Research Infrastructure Action under the FP6 Structuring the European Research Area Programme through the contract R II 3-CT-2004-506008. Technical assistance during x-ray fluorescence measurements at BESSY by R. Mitdank is gratefully acknowledged

REFERENCES

1. B.D. Beake et. al., J. Phys. D: Appl. Phys **39**, 1392-1397 (2006).
2. Y.G. Shen et. al., J. Mater. Res., **19** (2), 523-534 (2004).
3. F. Vaz et. al, Surf. Coat. and Technol. **146-147**, 274-279 (2001).
4. J.L. Endrino et. al., J. Mater. Res., **7** 3163, (2002).
5. S. Verprek, Thin Solid Films, **317** 449-454, (1998).
6. X.D. Zhang et. al., Surf. Coat. and Technol. **177-178**, 325-333 (2004).