Lattice Defect of Interfacial Layer in Superhard TiN/Si$_3$N$_4$ Multilayer Films Studied by Fluorescence X-Ray Absorption Fine Structure

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Abstract. Fluorescence x-ray absorption fine structure (XAFS) is used to study the local structures of super-hard TiN/Si$_3$N$_4$ multilayer films deposited by reactive magnetron sputtering at temperatures of 20, 200, 500 and 800 °C. The results clearly reveal the presence of interfacial intermixing between adjacent TiN and Si$_3$N$_4$ layers, composing of TiSi$_x$N$_{1-x}$ solid solution with a NaCl-like structure. With the growth temperature increasing from 20 to 500 °C, the thickness of interlayer rises from 2.5 to 5.0 Å. For the TiN/Si$_3$N$_4$ multilayer film grown at 500 °C, the interfacial layer is composed of TiSi$_{0.24}$N$_{0.76}$ solid solution, where the Ti-N bond length (2.07 Å) is largely shrunk as compared with the value (2.12 Å) in the pure TiN layer. When growth temperature rises to 800 °C, the composition of interfacial layer becomes TiSi$_{0.30}$N$_{0.70}$ and reaches the thickness of 7.8 Å. We propose that the TiSi$_x$N$_{1-x}$ interlayer with obviously contracted Ti-N bond length is an important hardening factor for the crystalline/amorphous TiN/Si$_3$N$_4$ multilayer films grown at high temperatures.

Keywords: Fluorescence XAFS, TiN/Si$_3$N$_4$ multilayer films, interlayer.
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INTRODUCTION

The crystalline/amorphous TiN/Si$_3$N$_4$ multilayer film is one of the important candidates for next-generation materials in high-temperature tribological applications[1] and protective coatings for cutting tools [2], because they possess qualities of super hardness (45 GPa)[2]. A number of studies have considered that the superhardness of TiN/Si$_3$N$_4$ multilayer film is strongly affected by the preparation conditions including the substrate temperature, the modulation period and modulation ratio[2-4]. To date, although different theories have been developed to explain the anomalous hardness enhancement in crystalline/amorphous multilayer systems, their hardening mechanism still remains an open question.

The recent studies [2,4] on the structure of TiN/Si$_3$N$_4$ multilayer films have displayed that the interfacial intermixing (namely interlayer) between TiN and Si$_3$N$_4$ layers may be one of the important factors influencing the superhardness. However, with TEM and XRD it is difficult to determine the chemical composition and atomic structure of the interface layer. Fortunately, XAFS is suitable to study the local structural information around a specified atom on the atomic level due to its sensitivity to the coordination environment [5].

In this paper, the fluorescence XAFS is used to investigate the structures of TiN/Si$_3$N$_4$ multilayer films fabricated by radio-frequency magnetron sputtering at different substrate temperatures of 20, 200, 500 and 800 °C. Our aim is to detect the lattice quality and understand the hardness enhancement mechanism in TiN/Si$_3$N$_4$ multilayer films influenced by the growth temperature. The XAFS results reveal that the interlayer is composed of a NaCl-like TiSi$_{1-x}$N$_x$ solid solution, whose thickness and Si concentration increase with the growth temperature. The observed Ti-N bond length shrinkage in the TiSi$_{1-x}$N$_x$ interlayer is responsible for the hardness enhancement in the TiN/Si$_3$N$_4$ multilayer films grown at high temperatures.
EXPERIMENTAL

TiN/Si3N4 multilayer films were deposited on Si(111) substrate maintained at the temperature of 20, 200, 500 and 800 °C, respectively, by a radio-frequency magnetron sputtering system. The other detailed description was reported in ref 3. The Ti K-edge XAFS measurements for the TiN thin film and TiN/Si3N4 multilayer films were performed at the beamline 4W1B of BSRF, Beijing Synchrotron Radiation Facility of China. The electron beam energy is 2.2 GeV and the maximum stored current was 100 mA. The monochromator is Si(111) plane double crystals. The X-ray harmonics were minimized by detuning the two flat Si(111) crystal monochromator to about 70% of the maximum incident light intensity. The Lytle fluorescence ionization chamber detector was used to collect the XAFS data of all the samples at room temperature, and the angle of incidence is 45°. The data analysis was performed using the NSRLXAFS3.0 software package.

RESULTS

Figure 1 shows the radial structural function (RSF) of the TiN thin film and TiN/Si3N4 multilayer films deposited at 20, 200, 500 and 800 °C. It can be observed that all the EXAFS oscillation curves of TiN/Si3N4 multi-layer films have a similar shape to that of TiN thin film except that the intensities of the oscillation peaks are different. It indicates that the coordination environment around Ti atoms in TiN/Si3N4 multi-layer films resembles that in TiN thin film and mainly maintains the medium-range order of NaCl-like structure of crystalline TiN. It also shows that the EXAFS oscillation amplitude for the TiN/Si3N4 multilayer samples increases remarkably with the growth temperature from 20 to 500 °C. However, as the growth temperature further increases to 800 °C, the EXAFS amplitude drops drastically by about 25% as compared with the sample grown at 500 °C. Since the EXAFS contributions of Ti–Si and Ti–N pairs are out-of-phase, their destructive interference decreases the EXAFS amplitude relative to that of TiN thin film. This is responsible for the lower EXAFS amplitude of the TiN/Si3N4 multilayer film deposited at 800°C as compared with that deposited at 500 °C. A similar phenomenon can also be found in Ti1-xSiNx compound film [8].

For the TiN/Si3N4 multilayer films fabricated by reactive magnetron sputtering in this work, the hardness values increase monotonically from 31 to 33, 38 and 40 GPa with the growth temperatures increasing from 20 to 200, 500 and 800 °C as reported elsewhere [3]. This result is in good agreement with Chen et al [2] and Leiste et al [7]. However, as shown in figure 1(a) and (b), the dependence of the EXAFS amplitude on growth temperature exhibits a different trend as the hardness does: at the substrate temperature of 500 °C the EXAFS amplitude is the maximum. The decrease in the EXAFS amplitude at the high growth temperature of 800 °C implies the occurrence of a strong interfacial intermixing. Similarly, the visible interfacial intermixing has also been observed previously by the TEM technique [2,7].

Based on the above results, we propose a model schematically shown in figure 2 to describe the real structure of the TiN/Si3N4 multilayer films. To simplify this model, we only consider the main interfacial intermixing occurring at the interface between the top of the TiN layer and bottom of the Si3N4 layer. This model is supported by the TEM and XRD results by Leiste et al [7], Vaz et al [8] and Carvalho et al [9]. In order to get quantitative results, we have fitted the first and second shell EXAFS peaks in the inversely Fourier transformed k-space. The theoretical back-scattering amplitude f(k) and phase shift δj(k) functions were calculated by FEFF7 code [10]. Two adjustable parameters x and p are used to relate to fit the coordination numbers. The obtained structural parameters are summarized in table 1.

FIGURE 1. The radial structural functions of TiN/Si3N4 multilayer films and TiN thin film.

FIGURE 2. Schematic model of TiSi1-xN1-x interlayer in TiN/Si3N4 multilayer films.
substrate temperature rises from 200 to 500 °C, and observable shrinkage from 2.11 to 2.07 Å as the hardness enhancement of TiN/Si3N4 multilayer films is more conceivable that the TiSi xN1-x interlayer increased hardness from 38 to 40 GPa. In this case it should have important impact on its hardness enhancement relative to the pure TiN layer. Moreover, for the TiN/Si3N4 multilayer film deposited at 800 °C with a high value of hardness (40 GPa), our result of the Ti-N bond length (2.06 Å) in the TiSi xN1-x interlayer is in good agreement with the value (2.045 Å) in SiTi2N4 compound[14], which was theoretically predicted to be a kind of super-hard material. Experimentally, a very high value of hardness (80–105 GPa) for Ti–Si–N nanocomposite films was also reported by Veprek et al[15]. On the other hand, from table 1 we can see that the difference between bond lengths $R_{Ti,N} = 2.06$ Å and $R_{Ti, Si} = 2.22$ Å is significant, which indicates strong lattice distortion of the Ti-Si-N interlayer, consistent with the higher $\sigma^2$ of Ti-N coordination in Ti-Si-N interlayer (0.0091 Å2) than in pure TiN layer (0.0065 Å2). Therefore, it can be expected that the Ti-Si-N interlayer with a NaCl-like structure can only exist in a very thin layer. This interlayer thickness is about 5.0 and 7.8 Å for the TiN/Si3N4 multilayer film grown at 500 and 800 °C, respectively. Chen et al have observed that the thickness of the interfacial intermixing layer is about 5.0–8.0 Å for the TiN/SiN4 multilayer film prepared by reactive magnetron sputtering and annealed at 1000°C.2

**CONCLUSIONS**

The fluorescence XAFS has been used to study the structure of TiN/SiN4 multilayer films fabricated at different temperatures. The XAFS results indicate that a strong interfacial intermixing occurs at the adjacent layer between TiN and Si3N4 layers at
higher growth temperatures of 500 and 800 °C. The interlayer of TiN/Si$_3$N$_4$ multilayer film grown at the temperature of 500 °C is composed of a TiSi$_{0.24}$N$_{0.76}$ solid solution with a thickness of 5.0 Å and a NaCl-like structure, where the Ti-N bond length (2.07 Å) is significantly shrunk as compared with the value (2.12 Å) in pure TiN layer. The presence of superhard TiSi$_{3-x}$N$_x$ interlayer with significant bond contraction has the effect of strengthening the hardness. For the multilayer films deposited at lower temperatures of 20 and 200 °C, the interfacial intermixing is small, so the crystal quality of pure TiN layer is the dominant factor responsible for the enhanced super-hardness with growth temperature.

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REFERENCES