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Effects of residual stress on the mechanical and structural properties of TiC thin films grown by RF sputtering

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Abstract

Titanium carbide thin films show attractive mechanical properties for engineering applications. Thin films of TiC were deposited on a ⟨100⟩ silicon substrate by RF sputtering from a TiC target. Various sputtering pressures were carried out in order to observe the influence of this parameter on structural and mechanical properties. The sputtering pressure was varied from 0.35 to 1 Pa at a sputtering power of 300 W. Rutherford backscattering spectroscopy (RBS), X-ray diffraction (XRD) and atomic force microscopy (AFM) were used to characterize TiC thin films. Hardness was obtained by nanoindentation. Residual stress was determined by radius of curvature measurements. Lower pressures induce the formation of a distorted titanium carbide and a dense structure. In correlation to the lower pressure, large residual stress was measured and changed the TiC texture in XRD results. Both the compressive stress and the hardness exhibited a maximum value at a process pressure using pure argon at 0.35 Pa with a pressure of 1 Pa necessary to obtain TiC films with ⟨111⟩ texture.

Keywords: RF sputtering; Titanium carbide; Thin films; TiC; Nanoindentation; X-ray diffraction; XPS; RBS

1. Introduction

Titanium carbide coatings are widely used in a variety of applications owing to their excellent properties, such as high thermal stability, high hardness and good corrosion resistance. Due to its high wear resistance and low friction coefficient, TiC is a important tribological coating. Typical applications include cutting, use as thermal barriers and for corrosion resistance on metallic structures.

Titanium carbide crystallizes in the NaCl-type structure similar to TiN, i.e. a cubic close-packed interstitial carbide. Stoichiometric TiC is obtained when a part of octahedral sites is occupied by carbon atoms, but it also exists under the form of various compositions essentially with carbon vacancies.

It is well known that the properties of deposited titanium carbide films depend strongly on the deposition conditions and elaboration methods. TiC thin films are obtained with several techniques such as PLD [1], CVD [2,3], evaporation [4] and sputtering [5–8]. Another study shows that properties of titanium carbide are related to their chemical composition [9–14], texture and result of low adhesion or residual stresses in the film.

In this paper, we present results on TiC films deposited without reactive gas, by means of RF sputtering and investigate the effect of the sputtering pressure on the structure, morphology and chemical composition. The mechanical properties of the deposited films were measured and compared to the residual stress.

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2. Experimental

2.1. Deposition technique

Titanium carbide thin films were produced by non-reactive RF sputtering from a stoichiometric TiC target (diameter of 12.7 cm) on ⟨100⟩ silicon wafers. The target substrate distance was kept constant at 7 cm and all the films were deposited with no heating and no bias polarization.

The initial pressure of the chamber was kept below 10^{-5} Pa before the deposition process. Total sputtering pressure was changed from 0.35 to 1 Pa at a sputtering RF power equal to 300 W. The film thickness was fixed at approximately 300 nm for mechanical studies.

2.2. Microstructural and mechanical characterization

The crystalline structure of the films was characterized by X-ray diffraction (XRD) using a Bruker d8 Advance X-ray diffractometer (Cu-Kα radiation). For XRD incident slit size is equal to 0.2 and 0.6 for detector slit size. For grazing XRD incident slit size is equal to 0.05 and 0.02 for detector slit size.

The composition of the films was determined using Rutherford backscattering spectroscopy (RBS). A microbeam of 1725 MeV H^+ ions was focused to the surface films under an incident angle of 10°, while H^+ ions backscattered by the target atoms were detected at a scattering angle of 170°. This incident energy has been chosen because Rutherford backscattering cross-section of carbon presents a resonant peak and so facilitates the evidence of carbon contained in surface thin films. The composition was obtained with an error of 5%.

XPS experiments were carried out at the "Nuclear Energy Division" of CEA, Saclay, France, by using a VG 220i Escalab XL spectrometer with a monochromatic AlK_α X-ray source (1486.6 eV). The collected photoelectrons are first selected in kinetic energy through an analyser and the signal is then magnified by six Channeltron detectors. Binding energy (BE) calibration was achieved using the Ag3d3/2 and Ag3d5/2 transitions (368.30 and 374.30 eV, respectively). The binding energy resolution of the spectrometer is estimated to be 0.1 eV. The BE position of the C_{1s} and Ti_{2p} photoelectron peaks was followed before and after the erosion of the surface. All the BE values were corrected by using the C_{1s} signal position of the contamination carbon at 285 eV. Erosion of the samples was obtained using an argon gun. Energy or Ar^+ was 4 keV with a current equal to 1 μA and erosion time close to 1200 s.

Atomic force microscopy (AFM) was performed to determine the surface roughness of thin films which is an important factor in the reproducibility and accuracy of nanoindentation measurements. All AFM measurements were done in the contact mode.

The mechanical properties of the TiC films were studied. The stress of the TiC films was determined by measuring (100) Si wafer curvature before and after the TiC deposition.

Common methods for experimental determination of residual stresses/strains include X-ray and neutron diffraction methods, Raman spectroscopy, and determination of shape (curvature) changes. The latter method is very suitable and widely used to assess residual stresses in layered materials and coatings. The advantage of the curvature measurement technique is that it provides rapid, cheap and uncomplicated measurements [15,16].

The strain and properties determined by curvature measurements are averaged over a large volume. This will contribute to a decreased scatter and need for less measurements as compared with diffraction methods. To determine curvature measurement, we used Fizeau interferometry.

The stress value of the TiC films was calculated using the Stoney formula [17]. Hardness measurements were carried out using a HYSITRON nanoindenter with a maximal force equal to 10 mN. A Berkovich diamond tip indenter was used. A simple loading–unloading cycle was used in all the experiments. All the data presented in this study corresponds to an average of 10 measurements. The indentation depth was never deeper than 10% of the total coating thickness to avoid the influence of the substrate. To determine the hardness, an Oliver and Pharr analysis was used [18].

3. Results and discussion

Fig. 1a shows the XRD patterns of films deposited at constant RF power of 300 W and at different sputtering pressures: 0.35, 0.5, 0.75 and 1 Pa. To analyse the different diffraction peaks, the ICCC-JCPDS Cards were used (titanium carbide no. 32-1383).

Films deposited at sputtering pressures of 0.35 and 0.5 Pa show two diffraction peaks corresponding to the (111) TiC, and a broader (200) peak.

When the pressure increases, the first peak shifts to a larger 2Θ position and reaches 2Θ=35.7 of TiC(111) [19–21] for 1 Pa. The width of the second peak decreases and shifts towards the position of the TiC(200) and disappears at 1 Pa. At 1 Pa only the (111) peak of TiC was observed in the XRD pattern.

In all cases, no graphitic carbon peak or amorphous carbon contribution was observed. Grazing X-ray diffraction was carried out on these samples with a grazing incidence angle of 1.4°. These diagrams (Fig. 1b) present a similar diffraction pattern and two other peaks (311) and (220) of TiC were observed. These peaks were not observed in X-ray diffraction (θ–2θ) owing to the high intensity of the silicon substrate diffraction peaks present in the same 2θ region. For films obtained with 1 Pa grazing X-ray diffraction results suggest that the films does not present a (111) texture which is in contradiction with XRD patterns. In fact, the grazing angle used for experiments and the large rocking curve observed for these films, which is a sign of great disorientation of the TiC grains, explain this result. Pole figure obtained in this film confirms the (111) texture.