Synthesis of TiN/a-Si_3N_4 thin film by using a Mather type dense plasma focus system*

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A 2.3 kJ Mather type pulsed plasma focus device was used for the synthesis of a TiN/a-Si_3N_4 thin film at room temperature. The film was characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and atomic force microscopy (AFM). The XRD pattern confirms the growth of polycrystalline TiN thin film. The XPS results indicate that the synthesized film is non-stoichiometric and contains titanium nitride, silicon nitride, and a phase of silicon oxy-nitride. The SEM and AFM results reveal that the surface of the synthesized film is quite smooth with 0.59 nm roughness (root-mean-square).

Keywords: plasma focus, TiN/a-Si_3N_4 films, X-ray diffraction

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1. Introduction

Titanium nitrides are extensively used in industrial applications such as hard protective coatings,[1,2] diffusion barriers in semiconductor technology,[3,4] optical applications in heat mirrors,[5,6] and decorative coatings[7,8] due to their excellent wear and corrosion resistance,[9] thermal stability,[10,11] chemical stability,[12] biocompatibility,[13] high hardness,[14,15] high melting point (2950 °C), and low friction coefficient. However, while in use, TiN coatings are degraded by oxidation at high temperature, so it is important to improve their oxidation resistance. As a possible solution to this problem, silicon atoms have been added to the TiN material, since TiN and Ti–Si–N have the same crystallographic structure (face-centered cubic).[16] In high temperature applications, an amorphous SiO_2 layer can serve as an oxidation barrier.[17] The Ti–Si–N shows promise as an ingredient of hard coatings because it has attractive physical and chemical properties, especially for high temperature use.[18,19]

The synthesis of different Ti–Si–N films has been reported with various deposition techniques including chemical vapor deposition,[20–23] ion beam assisted deposition,[24–27] and reactive magnetron sputtering.[28–30] The dense plasma focus (DPF)[31,32] is a potential hybrid deposition method. The plasma focus is an efficient source of X-rays, energetic ions, and relativistic electrons.[32] A plasma focus device is relatively simple and cheap, and offers advantages such as energetic ion assisted deposition and higher deposition rates. Films deposited by plasma focus devices have superior surfaces owing both to the devices' broad ion energy spectrum and the grain growth of different compounds through nucleation by successive focus shots at room temperature environment. The DPF deposition can produce a denser coated layer in less deposition time. It does not need extra substrate heating during film deposition because the substrates are heated during ion beam treatment, unlike other treatments.

Successful uses of the plasma focus as an ion source for material processing, surface modification, and thin film deposition have been demonstrated by many researchers.[33–37] Feugeas *et al.*[36] first used a low energy plasma focus as a pulse ion implanter. Kelly *et al.*[37] produced a TiN thin film well-adhered to a stainless steel substrate. We previously reported the deposition of titanium nitride on Si(100) wafers using plasma focus.[38] In that experiment, we used titanium as the target material and silicon as the substrate material. In the experiment presented in the present paper, we interchange the target (titanium) with the substrate (silicon) materials and find completely different results. In this work, silicon is used as the target material in a plasma focus device for the first time, to the best of our knowledge.

A TiN/a-Si_3N_4 film is prepared using a dense plasma focus system. The film is prepared at 90 mm away from the top of the anode and at zero angular position with respect to the node axis with five deposition focus shots. The chemical composition, microstructure, surface morphology, and surface roughness of the thin film are also analyzed.

2. Experimental setup and methodology

For the synthesis of the TiN/a-Si_3N_4 film, polished 10 mm×10 mm×5 mm titanium was used as the substrate. The substrates were cleaned by rinsing in an ultrasonic bath

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of water. The deposition process was performed in a Mather-type DPF device powered by a single 32 μF, 15 kV capacitor. Details of the plasma focus device were given in the earlier work.[32] The schematic diagram of the system is shown in Fig. 1. The conventional Mather-type plasma focus electrode assembly has a hollow copper anode surrounded by six cylindrical copper cathode rods in a squirrel type cage. For the synthesis of the Ti–Si–N film, a copper anode with a silicon insert fitted on the top was used. Nitrogen was used as the working gas. The chamber was evacuated down to 1×10^{-2} mbar by a rotary vane pump and filled with high purity nitrogen gas before the plasma focus operation. The focusing action was monitored using a simple resistive voltage probe and a Rogowski coil. An intense voltage spike in the high voltage probe signal and a steep current dip in the Rogowski coil together were the indicater of the strong focusing action, which ensured efficient energy transfer and heated the plasma column. The substrate was mounted at a fixed distance of 9 cm away from the top of the anode using a substrate holder behind a moveable metallic shutter (shown in Fig. 1). A qualitative account of the film deposition process in the dense plasma focus device is as follows. The DPF transfers the electric energy stored in the capacitor to the chamber by a spark gap switch. The dielectric breakdown of gas occurs along the insulator surface in between the anode and the cathode, and an axisymmetric current sheath forms around the insulator. This current sheath moves toward the open end of the electrode assembly under the magnetic force. When this current sheath reaches the top of the electrode assembly, it collapses radially inward during the final focus phase. This is the instant when micro instabilities, mainly $m = 0$ instabilities, start to grow and in turn enhance the induced electric field locally. This enhanced electric field, coupled with the magnetic fields, breaks the focused plasma column by accelerating ions toward the top of the chamber and electrons toward the positively charged anode. After this, the disruption of the plasma column starts, and it breaks up completely to form hot (1–2 keV), dense (10^{25}–10^{26} m^{-3}) plasma.

In the present work, the TiN/a-Si_3N_4 film was synthesized with five focus shots. The crystalline structure of the film was characterized by X-ray diffraction (XRD) using an X'Pert PRO MPD X-ray diffractometer. The chemical composition was identified using X-ray imaging photoelectron spectrometer Axis Ultra (Kratos Analytical). The surface morphology and roughness were examined by a JEOL JSM 840A scanning electron microscope (SEM) and a Pico SPM atomic force microscope (AFM), respectively.

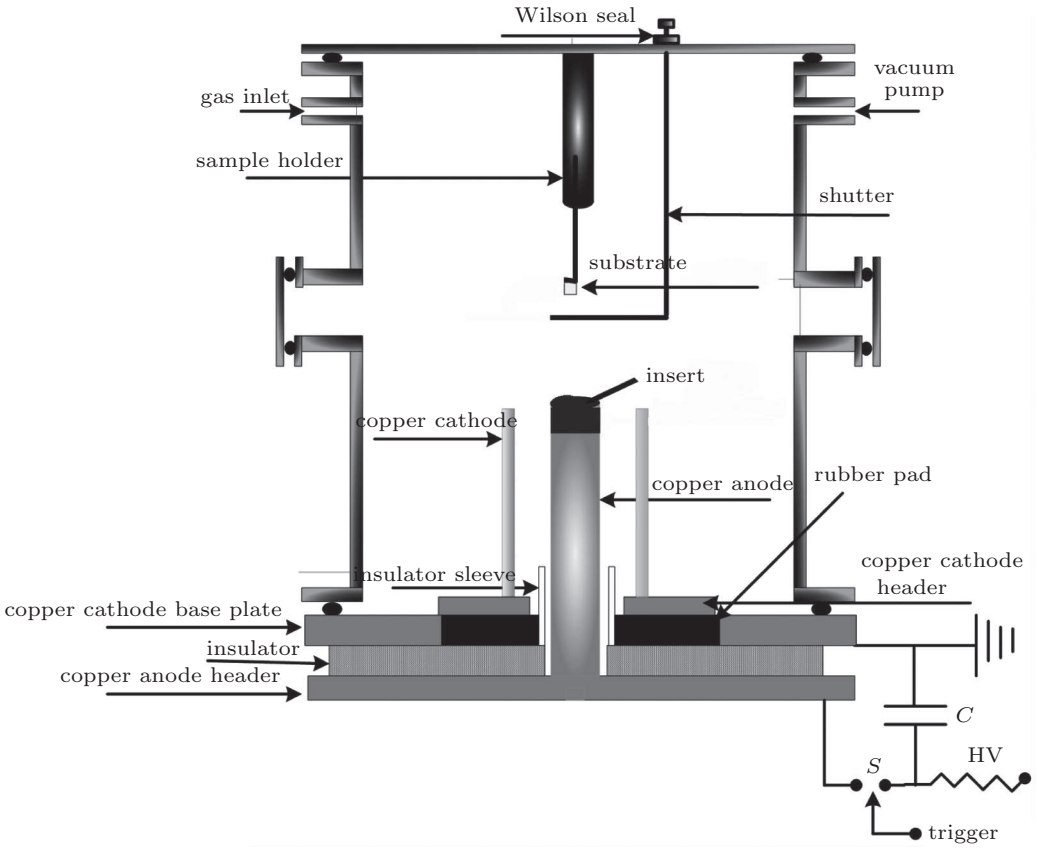


Fig. 1. Schematic diagram of dense plasma focus device.

3. Results and discussion

3.1. X-ray diffraction analysis

XRD measurements were made at a grazing incidence angle of 2°, with the machine operating at 40 kV, 40 mA and employing the Cu K_α radiation. Figure 2 shows the X-ray diffraction patterns of untreated and treated samples at room temperature and at the zero angle position for five focus shots. Figure 2(a) shows the titanium peaks of an untreated sample. In the treated sample, the peaks at 36.8°, 42.61°, 61.98°, 74.311°, and 78.077° correspond to (111), (200), (220), (311), and (222) of crystalline TiN, as shown in Fig. 2(b). No reflection peaks assigned to Si_3N_4 or other titanium silicide phases are observed. This implies that either silicon is not incorporated into the film, or silicon is present in an amorphous phase of silicon nitride or silicon oxy-nitride. These findings are in agreement with the previous observations of nc-TiN/a-Si_3N_4 films deposited by DPF.[38]

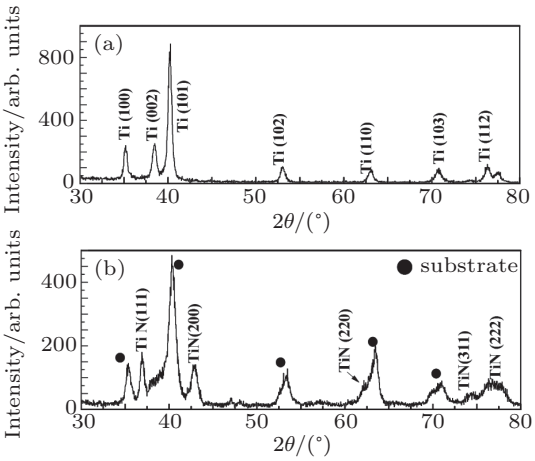


Fig. 2. XRD patterns of (a) untreated titanium and (b) thin film deposited at a distance of 9 cm at zero angular position with five focus shots.

Two predominant processes occur in the titanium substrate in the DPF during the film deposition. (i) Nitrogen ions accelerate toward the titanium substrate and hit the surface, causing high thermal gradients due to the fast energy transfer. Consequently, high heating and cooling rates develop in the surface layer of titanium. These nitrogen ions etch and clean the substrate surface besides synthesizing the film. Then the nitrogen is implanted, forming the TiN phase. (ii) Electrons accelerate toward the silicon anode, and ablate the material from a node. The ablated silicon material can either directly become imbedded in the titanium substrate or, most likely, interact with the reactive nitrogen ions of the same shot to form silicon nitride and become adsorbed on the titanium substrate. In a single focus shot, the ions of the filling gas are emitted in the form of micro beams in more than one bunch with a duration of a few nanoseconds.[39] The nitrogen ions from the next shot can also react with the deposited silicon atoms, resulting in more Si_3N_4 in the film. It is difficult to distinguish the two i.e., the formation of Si_3N_4 during the same focus shot or during the next focus shot. However, it is reasonable to assume that most of the silicon ions and atoms in ablated plasma will be able to combine with nitrogen to form Si_3N_4. The synthesized film, therefore, primarily contains titanium nitride along with a Si_3N_4 layer.

Each focus shot results in the exposure of the sample to a pulsed energetic ion beam (with pulse duration of about 100 ns having ions in the energy range from 38 keV to 1.6 MeV), heating the substrate surface up to several thousand degrees in a very short time.[38] This provides a high surface mobility, which helps the silicon migrate toward the grain boundaries of the transition-metal nitride. An Si–N phase nucleates and obstructs the formation of the metastable Ti–Si–N solid solution phase. The presence of this amorphous phase can contribute to fixing the boundaries of the nanocrystallites, thus limiting their growth.[39,40] This segregation of TiN and silicon nitride phases forms a nanocomposite film of the type nc-TiN/a-Si_3N_4. Thus the ion irradiation process is equivalent to transient thermal annealing and rearranging atoms in the surface layer, leading to the formation of nanoparticles.

In addition, the lattice parameter of crystalline TiN in our TiN/a-Si_3N_4 thin film, calculated from the (1 1 1) inter-planar distance, is 4.43 Å, which is a little larger than that obtained from powder-diffraction files (PDF) (4.40 Å).[41] This is because a compressive stress is induced in the coating by the ion bombardment during the deposition process. It can be concluded that the solid solution phase did not form in this thin film. This is also confirmed by the XPS results presented in the following section.

3.2. XPS analysis

XPS was performed to investigate the bonding statuses of Si and N in these films as represented in Fig. 3. XPS is used to obtain extensive information about the chemical structure and the bonding states in the outermost surface of the synthesized thin film. XPS spectra of the deposited films clearly show the presence of titanium, silicon, nitrogen, oxygen, and carbon. However, a large amount of oxygen and carbon are found on the surface. During the XPS analysis, it is a common practice to ion etch the sample surface. This practice arises due to the fact that XPS samples as-inserted always have carbon and oxygen on the surface unless they have been prepared in ultra-high vacuum and have not been exposed to air. A gradual reduction of oxygen and particularly carbon within the XPS analysis depth can be seen in the XPS spectra if the sample is etched with the argon gas before analysis. Oxygen, on the other hand, is present at the surface of our synthesized film.

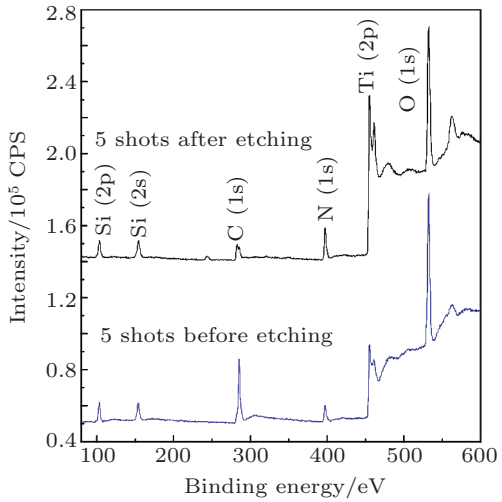


Fig. 3. (color online) XPS spectra obtained before and after 1 min of 4 kV sputtering with Ar^+ ions for the film deposited with five focus shots.

Another feature of the photoelectron spectra, the splitting of the Si 2p and Ti 2p lines, is analyzed to investigate the different silicon- and titanium-containing chemical compounds present in the film. In Fig. 4(a), the Si 2p peak can be readily de-convoluted into two components, indicating that silicon exists in the thin film as Si_3N_4 (appearing at 101.9 eV) and oxygen-rich SiON (appearing at 102.8 eV) without detectable $TiSi_x$ or un-reacted Si. The Si 2p binding energy of $TiSi_2$ is 98.8 eV.[39] No peak at the binding energy of 98.8 eV is observed.

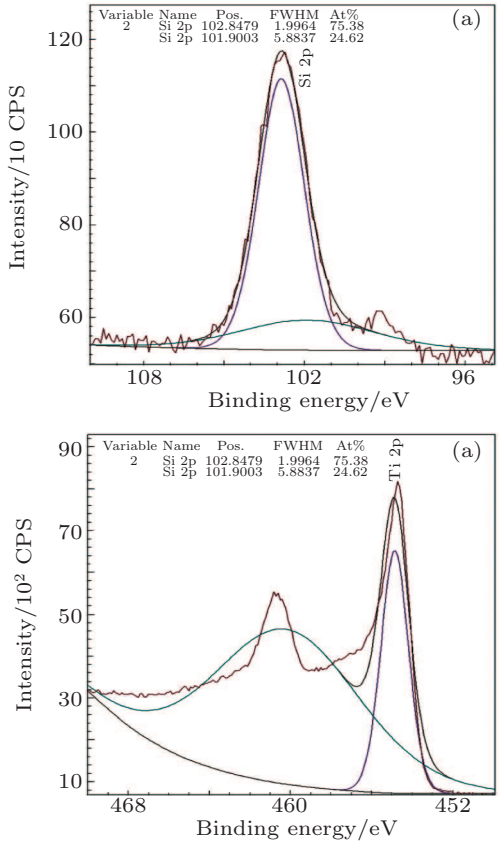


Fig. 4. (color online) XPS spectra of (a) Si 2p peak (b) Ti 2p peak for five focus shots.

The titanium 2p peak in Fig. 4(b) shows a complex structure that can be attributed both to the presence of several phases in different amounts, i.e., titanium nitrides, oxides, and oxynitrides in a wide range of stoichiometries, and to their energy loss peaks. Titanium nitride phases can be identified by the $2p_{3/2}$ peak at 454.8 eV and the $2p_{1/2}$ peak at 460.2 eV. The other components of the Ti $p_{3/2}$ peak due to oxide ($\sim$ 458 eV), and energy losses ($\sim$456 eV) cannot be resolved in the collected spectra. The XPS analysis around the Si 2p and Ti 2p lines indicates that, at the surface of the synthesized thin film, both Ti and Si are oxidized. As XPS provides information only about the uppermost monolayers of the film, the relatively large SiO_xN_y content measured in our experiment can be explained by the oxidation of the surface.

3.3. Surface morphology

SEM micrographs revealing the surface morphologies of the titanium sample and the sample exposed to five focus shots at the 9 cm axial and 0° angular position are shown in Figs. 5(a) and 5(b), respectively. The unexposed sample surface shows polishing marks that have been covered by the TiN/a-Si_3N_4 film in a treated sample. The micrograph of the synthesized thin film shows an almost smooth layer with fine grains uniformly covering the surface. The DPF ion bombardment results in a restructuring of the substrate surface during collision cascades along with the interstitial implantation of nitrogen ions and the formation of the TiN compound. The reaction of ablated Si with the electrons of gas phase nitrogen forms an Si_3N_4 compound, which is deposited on the substrate.

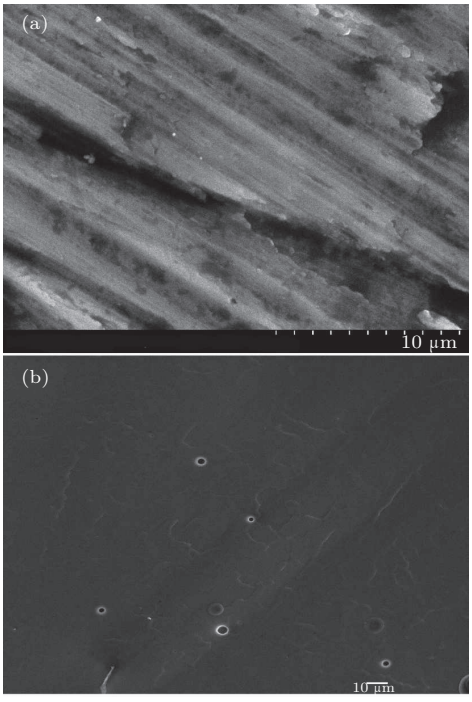


Fig. 5. Scanning electron micrographs of (a) untreated and (b) treated with five focus shots titanium.

3.4. Roughness measurement

AFM studies were carried out to investigate the surface morphology and the roughness of the synthesized film. The film was scanned on four random surface areas to check the consistency of the images. The sampling area was 5 μm × 5 μm. Figure 6 presents three-dimensional AFM surface morphology of the thin film deposited with five focus shots. The root-mean-square (rms) surface roughness of the film was evaluated. The observation of the AFM micrograph indicates a dense, smooth surface. The surface roughness is 0.58 nm, it is much smoother than plasma focus deposited thin films reported previously.[38]

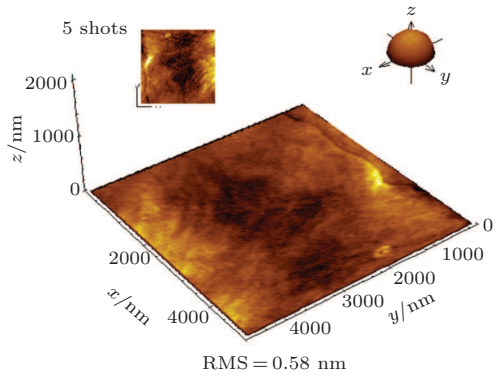


Fig. 6. (color online) Root-mean-square surface roughness and atomic force micrograph of the film synthesized with five focus shots. Inset shows the micrograph in a different view.

4. Conclusions

In summary, we synthesized a TiN/a-Si_3N_4 film at room temperature with five focus shots using a dense plasma focus system. The microstructure, chemical composition, surface morphology, and roughness of the film were investigated through XRD, XPS, SEM, and AFM. XRD results confirm the deposition of polycrystalline TiN thin film. SEM results show a dense, amorphous, compact structure almost without any obvious defect. AFM images show that the film surface is much smoother than plasma focus deposited thin films reported previously.

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