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Crystalline carbon nitride film synthesized by ion beam assisted magnetron sputtering and thermal annealing in nitrogen gas

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ABSTRACT

Crystalline carbon nitride film has been successfully prepared by the ion beam-assist magnetron sputtering and the following thermal annealing in N_2. The microstructure of the carbon nitride film is investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The film contains a very dense and homogenous distribution of crystalline grains, the lattice parameters of the crystalline phase are in good agreement with those theoretically predicted β-C_3N_4, and X-ray photoelectron spectroscopy (XPS) analysis also supports the existence of sp^3-hybridized C–N bonds in the film. The fractional concentration of the crystalline carbon nitride particles in the film is 43.91% and the N/C ratio of the crystalline carbon nitride particles is 1.44, obviously higher than those in previous works.

1. Introduction

β-C_3N_4 is a hypothetical super hard material predicted by ab initio calculation and confirmed by Cohen and his coworker [1,2]. Since then, many scientists tried to synthesize it in the laboratory through various methods [3–5]. After years of hard work, some progress has been made in both theoretical calculations and experimental synthesis [6–10]. However, the formation of high pure crystalline β-C3N4 is not confirmed yet. In most cases, the grown carbon nitride films were seriously nitrogen deficient compared with stoichiometric β-C_3N_4 [11–20]. It is still a challenging topic for preparing carbon nitride films with high crystallinity and high nitrogen content by experimental method.

In our previous work [21], we have reported the formation of nanocrystalline carbon nitride films deposited on Si substrates by a combination of direct current magnetron sputtering and thermal annealing under Ar. TEM, Raman measurements and XPS spectra of samples strongly support the formation of β-C_3N_4 in the films, the fractional concentration of β-C_3N_4 crystalline phase in the carbon nitride film was up to 42%, and the crystallinity of the film was distinctly improved as compared with other works. Thus, we suggested two strategies to promote the formation of crystalline β-C_3N_4 films. One is the requirement of low temperature deposition processing to retain a high N content in the film, the other is the requirement of high temperature to meet the growth condition for crystalline carbon nitride.

In this present work, we made a great improvement based on our previous work, the previous prepared methods are replaced by a new two-step method, composed of ion beam assist magnetron sputtering deposit and thermal annealing in N_2 was proposed to meet the above two strategies. On one hand, the ion beam assist magnetron sputtering was used to synthesize amorphous carbon nitride film on TiN coated Si substrate. The nitrogen ion beam assist magnetron sputtering has been widely used in preparing CN_x films, which can effectively decompose and ionize nitrogen molecules, and make energetic nitrogen ions that are essential to the formation of carbon nitride film with high sp^3 C bonding and high N content. On the other hand, the as-deposited film with high sp^3 C bonding and N content was annealed in N_2 atmosphere to obtain a relatively stable phase. It is believed that a thermal stable crystalline carbon nitride phase may be formed by the high temperature thermal treatment. Indeed, using the annealing, the transformation of amorphous to crystalline structure had been observed in the previous work [21]. This is a new growth mechanism for metastable crystal growth though relatively stabilized experimental method. According to this proposal, we have synthesized high pure crystalline β-C_3N_4 films by new two step method, and the microstructure of the crystalline carbon nitride films is also discussed in details.

2. Experiment details

The carbon nitride film was deposited on single crystalline Si (100) wafers by ion beam assist magnetron sputtering with a pyrolytic graphite target (76 mm in diameter) in pure nitrogen atmosphere. The ion beam system consisted of a 3 cm Kaufman-type ion source with Ar

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ion energies of 350–1250 eV, and the ion beam source was at an incidence of 45° to the target. The distance between the substrates and the targets was 8 cm. The Si substrates were cleaned with acetone, methanol and briefly immersed in dilute HF to remove the surface oxides. Prior to deposition, the chamber was vacuumed to a base pressure of 3×10^{-3} Pa, and then the nitrogen stream was introduced to keep the process pressure at 0.25 Pa. The work targets were cleaning lasting for 10 min, and the substrates were etched for 30 min by sputtering at a substrate bias of −250 V and a sputter current of 0.07 A to remove the oxides and adsorptions in the same chamber, and followed by depositing a 10-nm thick TiN underlayer. During the deposition of TiN layer, the substrate temperature was maintained at 625 K, and the voltage was kept at 300 V and the corresponding current was 0.2 A. Then the required carbon nitride film was deposited on the TiN underlayer. During the deposition of carbon nitride film, the substrate bias of −220 V was applied for the ion bombardment towards the film, and the substrate temperature was also maintained at 350 K. The film was deposited at a voltage of 550 V and a sputter current of 0.35 A. Under such condition, a 300-nm thick film was obtained after deposition for 1 h.

High-temperature thermal annealing was carried out in a quartz vacuum chamber in pure N_2 gas. Radio frequency induction heating at 500 kHz enabled the temperature to be ramped up to 1000 K within 5 min and the as-deposited film was heated in this manner at 1000 K for different times before being cooled down to room temperature. The morphology and microstructure of the as-deposited and annealed films were examined using a Tecnai G2 F30 analytical transmission electron microscope (TEM) operating at 300 kV and X-ray diffraction (XRD, Philips PC-APD with Cu Kα radiation).

The bonded structure of the annealed film was characterized by X-ray photoelectron spectroscopy (XPS) using an ESCALab 220i-XL electron spectrometer, operating with a monochromated Al-Kα X-ray radiation source in a base pressure of 10^{-7} Pa. The binding energies were referenced to the C 1 s line at 284.6 eV from adventitious carbon.

3. Results and discussion

3.1. TEM observation

Fig. 1a shows a typical TEM image of the as-deposited carbon nitride film. The selected area electron diffraction (SAED) pattern inserted in the upper left-hand side of the photograph presents that the film is in amorphous state. Fig. 1b shows the Plan-TEM image of the carbon nitride film after thermal annealing in the presence of N_2 gas at 1000 K for 1 h. It is found that the crystalline particles with several nanometers have been grown in the annealed film. These crystalline particles are thermally stable since they appear after annealing. EDX analysis indicates that the chemical composition ratio for N:C is about 1.33, which is in good agreement with the stoichiometric composition of C_3N_4. Besides, an amorphous phase exists in the film. It is also found that the structural size of crystalline particles increases with the annealing time, leading to a nanosphere-like structure. Fig. 1c presents a representative TEM image of the nanospheres from the film after thermal annealing for 2 h. These particles are perfectly round and smooth, in a highly homogeneous arrangement. The estimated content of nanocrystals is up to 45% in volume from Fig. 1c, which is consistent with the results of the following XPS analysis, obviously higher than that in the previous work [21].

In order to determine uniquely the structure of the crystal. Fig. 2a shows the cross-TEM image of the film after thermal annealing in pure N_2 gas for 1 h. It is clearly seen that the film is continuous and flat over that the large field of view. The film contains two layers, TiN and carbon nitride layer. Obviously, some polycrystalline clusters with several nanometers can be seen in the HRTEM image (Fig. 2b), which are surrounded by the other crystalline clusters. The lattice planes go straight through the interfaces between the particles, which means that the particles fused together. A typical electron diffraction pattern

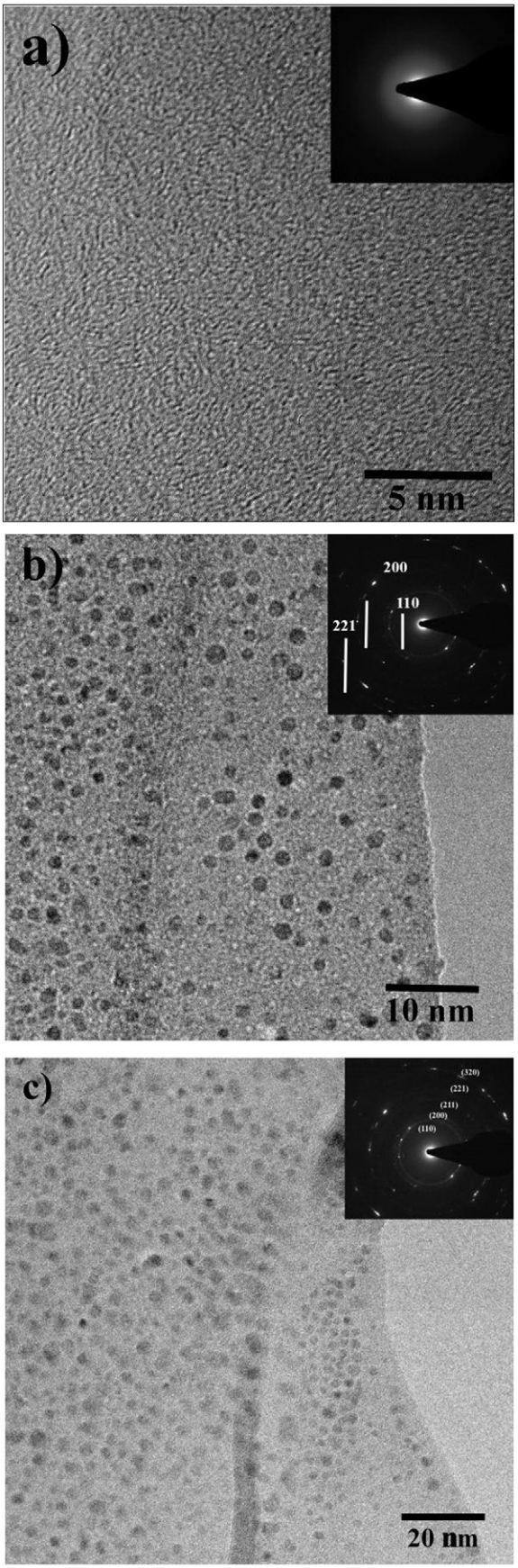

Fig. 1. (a) Low-magnification Plan-TEM images of the as-deposited carbon nitride film, Plan-TEM of the carbon nitride film after annealing for 1 h (b) and 2 h (c).