Vacuum 125 (2016) 36–39

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Short communication

Interface features of carbon nitride films deposited on Si substrate

D.G. Liu [a, *], W.Q. Bai [b], Y.J. Pan [c], J.P. Tu [b, **]

[a] Center of Composite Material and Surface Treatment, China Electronic Technology Group Corporation No. 38 Research Institute (CETC 38), Hefei 230031, China
[b] State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China
[c] Computational Mechanics Group, INSIA, Universidad Politécnica de Madrid, Ctra. Valencia km 7, Madrid 28031, Spain

ARTICLE INFO

Article history:
Received 9 September 2015
Received in revised form
27 November 2015
Accepted 1 December 2015
Available online 9 December 2015

Keywords:
Carbon nitride
Magnetron sputtering
Mismatch
Interfacial layer
Stress

ABSTRACT

One kind of super-hard a-CN_x film was deposited on Si substrate by the ion-beam assist magnetron sputtering. A clear interfacial layer with homogeneous thickness was found in the as-deposited film. The a-CN_x layer spontaneous spalled along the interfacial defect, which indicated a high internal stress, resulting in adhesion failure. After thermal treatment, the interfacial layer between Ti layer and Si substrate seem to present a coherent or semi-coherent type with some misfit at the Si/SiO_x grain boundaries. This mismatch relaxed the strain of the interface defects, and the high internal stress of the film was induced with a 3–5 atom-thick strained layer on Si substrate.

Recent years, ion beam assist magnetron sputtering techniques have been successfully applied to deposit the CN_x films with high N content, but ion beam bombardment additionally induces an undesirable high intrinsic stress in the growing films [1–5]. Consequence, the CN_x films delaminate when their thickness exceeds hundreds of nanometers. Post-growth thermal annealing treatment and fabrication of composite multilayer structure CN_x film can solve this problem [6–11]. Especially in later case, the state of the interfaces between the single layers and the substrates is the major importance to the stability and mechanical performance of the whole films. The formation of interface zones between the substrate and film, or between the single-layer of multilayer is one of the decisive implications for the film adhesion [12–14]. However, the experimental evidences for film delaminating with an increased defect density and high stress are still scarce. The aim of this work was focused on the atomic scale analysis of the interfaces characteristic in the CN_x films. The structural results are also discussed in relation to the mechanical properties.

Ion-beam assist magnetron sputtering system was employed to prepare a-CN_x films on Si substrates. Details about the machine configurations were introduced elsewhere [15]. N_2 mixed with Ar gas was used as working gas to control the N content in the films at a fixed working pressure of 0.32 Pa. Two kinds of films named film A (without thermal treatment) and film B (with thermal treatment) were prepared. Details of experimental parameters and composition of films are displayed in Table 1. Meanwhile, the pure a-CN_x film was also prepared for comparison. The buckling process of the film was observed by an optical microscope. The microstructure observation of films was carried out with a Tecnai G2 F30 S-Twin analytical transmission electron microscope. Microstructure analyses were performed by applying fast Fourier transform (FFT) analysis.

Fig. 1 shows the load–displacement curves of the CN_x films. From this measurement, film B that with thermal treatment shows a hardness value of 31 GPa, which is obviously lower than that of the a-CN_x film A (40 GPa) without heat treatment. The stress of film B (2.45 GPa), which is lower than the value of film A (5.38 GPa), the stress level has reduced by 3 GPa though the heat thermal treatment. This behavior may have the following explanation: though the thermal treatment, the sp^3-rich CN_x layer relaxes the high stress of the interface defects, and thus affects the mechanical properties in the film. It is speculated that the formation of multilayer structure composed of the uniform transitional layers for the film A is difficult, and therefore, the film A has the clear interfaces and exhibits high hardness and stress value.

* Corresponding author.
** Corresponding author.
E-mail addresses: liudongguang2007@163.com (D.G. Liu), tujp@zju.edu.cn (J.P. Tu).

http://dx.doi.org/10.1016/j.vacuum.2015.12.001
0042-207X/

Table 1
Details of experimental parameters and composition of film.

Film	Current (A)	sp^3/sp^2	Modulus (G Pa)	Hardess (G Pa)
Pure a-CN_x	0.3	1.86	181	21.9
Film A	0.3	2.37	289	40
Film B	0.3	2.12	231	31

Fig. 2a shows the OM image of film A. The image reveals the CN_x film (thickness 300 nm) delaminated, and proceeded by the propagation of the blister edge along the a-CN_x/Ti/Si interface. The a-CN_x film spalling process should be preceded by buckling process above interfacial defects [16], such as void, or some other defects, causing random formation of voids defect, marked in Fig. 2b. When the accumulation compressive stress inside the films reaches a critical value, film buckling will occur above the interfacial defects, then the compressive stress in the buckled region is partially relieved.

The cross-section TEM image of the t = 300 nm sample (Fig. 3a) shows that film A is continuous and flat over the large field of view. The film contains several layers, like flue layer, Ti layer and carbon nitride layer. From Fig. 3b, a clear interfacial layer with homogeneous thickness along the film growth direction is observed at the Si/CN_x interface. The interface zone with different contrast is also observed, and the thickness of the SiO_x interfacial layer is about 3 nm, as marked in Fig. 3b. The measured d-spacings from the diffraction ring of the interfacial layer match well with the values from Si substrate. These measurements exclude the presence of significant impurities of titanium buffer layer. Electron diffraction pattern of the SiO_x interfacial layer and Ti layer shows amorphous quality, except some alternating distinct types of defects are observed in the interface zone, as shown in Fig 3b. Fig. (3c and d) show a two dimensional resolution by visualizing one set of Si crystal planes (near interfacial layer) using Bragg, the changes of lattice parameters in Si/substrate were studied. The results indicate that there are no obviously changes for all lattice parameters near the interface. A Burgers circuit vector is drawn in Fig 3d. It confirms there is no dislocation close to the interface, thus, there is no strained layer appearing in the film interface. For film A, the slip of misfit dislocations scarcely exist since its amorphous microstructure, thus, the interface defects play an important role in the coating adhesive, stress relaxation, resulting in the buckling and the spalling of the film [17,18].

Fig. 4 shows the TEM image of film B. From Fig. 4a, difference of contrast is confirmed in interfacial layer, which is not uniform in thickness, being thicker than 2 nm in some zones, whereas in others exist continuity of atomic columns between Si substrate and Ti layer. These observations suggest that SiO_x layer grow on Si (001) substrate by a lateral epitaxial growth process as marked shown in Fig 4b. We note that Ti layer with the presence of SiO_x interfacial layer shows high crystalline quality, whereas complete reduction of this SiO_x layer in thickness. The interfacial layer seems to present a coherent or semi-coherent type with some misfit at the Si/SiO_x grain boundaries (in Fig. 4), and the film appears a strained layer on Si substrate in film/substrate interface, which thickness is 3–5 atom layer. By visualizing one set of crystal planes using Bragg, the changes of lattice parameters at the interface in Si substrate were studied (Fig. 4c and d). The results show that there are sharp changes near the Si interface for all the lattice parameters. Furthermore, the changes of lattice parameters in film B are higher than those films without thermal treatment. The in-plane lattice parameter is smaller by around 23.8% for silicon substrate, whereas the Si/Ti film is relaxed as indicated by the deformation of around 25% (note that close to the interface cannot be accurately calculated). Thus, intermediate layer between substrate and film likely helps to accommodate the large lattice mismatch of around 25% between Ti layer and Si substrate. This mismatch could explain the presence of misfit dislocations to relax the strain at the interface.

As above depicted, interface defects and strained layer appearing in the film B interfaces could be account for the reduction of the compressive stress. The defective regions present an in-plane lattice parameter intermediate between Si and the film, and thus can help to release the stress associated to the interface between crystalline Ti layer and Si. For the multilayer film B, the defects number of interface is larger, and the total energy is lower than film A. This energy minimization is particularly strong near the

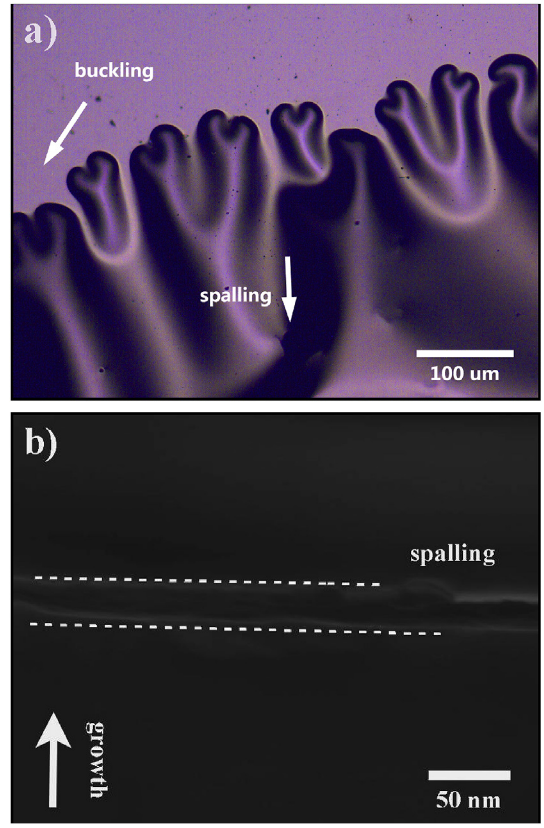

Fig. 2. OM (a) and SEM (b) images of the spontaneous buckling for film A deposited on silicon substrate.

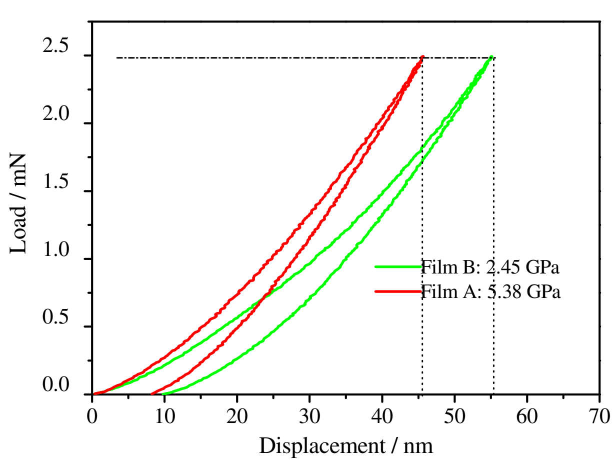

Fig. 1. Typical load–displacement curves for the a-CN_x films using a maximum load of 10 mN.