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Adhesion properties of nitrogen ion implanted ultra-nanocrystalline diamond films on silicon substrate

U.A. Palnitkar [a], P.T. Joseph [b], H. Niu [c], H.Y. Huang [d], W.L. Fang [d], H.F. Cheng [e], N.H. Tai [b], I.N. Lin [a,*]

[a] *Department of Physics, Tamkang University, Tamsui 251, Taiwan, ROC*
[b] *Department of Materials Science and Engineering, National Tsing-Hua University, Hsin-Chu 300, Taiwan, ROC*
[c] *Nuclear Science and Technology Development Center, National Tsing-Hua University, Hsin-Chu 300, Taiwan, ROC*
[d] *Department of Power Mechanical Engineering, National Tsing-Hua University, Hsin-Chu 300, Taiwan, ROC*
[e] *Department of Physics, National Taiwan Normal University, Taipei 116, Taiwan, ROC*

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Abstract

Ultra-nanocrystalline diamond (UNCD) films prepared by microwave plasma enhanced chemical vapor deposition were implanted using 0.3 MeV nitrogen ions under a dose of 10^{13}, 10^{14}, and 10^{15} ions cm^{-2}. While the surface morphology of the UNCD films was not pronounced modified, the crystallinity of the films was changed appreciably due to ion implantation. The scratch test has been used to study the adhesion of the film to the substrate, which illustrated that the critical load, used as a measure of the adhesive strength, is found to increase with ion dose. Secondary ion mass spectroscopy (SIMS) analyses on the interfacial morphology indicated that the main factor in improving the adhesive strength is the modification on interfacial structure through inter-diffusion between film and substrate.

Keywords: UNCD; Adhesion; Ion implantation; Interface structure

1. Introduction

Ultra-nanocrystalline diamond (UNCD) film is a promising material for numerous applications, because of its remarkable mechanical, optical, thermal, dielectric properties low threshold value for field emission, and a wide electrochemical potential window. These properties have increased the interest in potential application in electronic industry, such as p–n junctions, field emitters and biosensors. This is especially true when taking into account that the surface of the as-grown UNCD film is already very smooth and there is no need to post polish it. An obstacle to the wide applicability of diamond film is associated with poor adhesion with substrate due to high residual stress inherent in the films [1–3]. It has been reported by many authors that as-grown nanocrystalline diamond films have high residual stress [4–6], which may cause cracks in the film or film peeling from the substrate. High residual stress can directly influence the long term operation performance and reliability of the devices. Therefore, understanding and controlling the residual stresses of diamond films and improving the adhesion to the substrate are of great importance both for scientific and industrial view. Since such an inherent stress could be one of the reasons of poor adhesion of the film to the substrate, the current research in this area in various laboratories and universities is aimed to reduce this stress and at the same time improve adhesion of these films with the substrate [6–8]. Ion beam can improve adhesion even at the interface where no chemical affinity exists between the film and the substrate. The ion irradiation technique of adhesion improvement has found use in technologically improvement couples such as metal–polymer, metal–glass and metal–ceramics required in semiconductor industries. Ion beam energies ranging from few keV to MeV to a few GeV have been used [9–16].

In the present paper we have used ion implantation as one of the method to improve the adhesion of the film with the substrate.

* Corresponding author. Tel.: +886 2 26268907; fax: +886 2 26209917.
E-mail address: inanlin@mail.tku.edu.tw (I.N. Lin).

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We have studied the effect of nitrogen ion irradiation, in the dose 10^{13} to 10^{15} on ultra nanocrystalline diamond films deposited on silicon substrate. The possible mechanism which improved the UNCD to silicon adhesion was investigated.

2. Experimental details

Ultra Nanocrystalline diamond films of about 330 nm thickness were prepared on silicon substrates; using microwave plasma enhanced chemical vapor deposition (MPECVD, IPLAS, CYRANNUS, 2.45 G Hz) process on silicon. Pretreatment of substrate was performed by ultrasonication in nanosized diamond and titanium powder containing methanol solution for 45 min, which we have found an efficient pretreatment process for the growth of UNCD by creating nucleation sites with highest number density. Then the substrates were cleaned using methanol and DI water respectively. The deposition pressure was maintained at 120 Torr and deposition was carried out in CH_4/Ar medium (1:99). The UNCD growth process was carried out at low temperatures (<465 °C) without heating the substrate. Ion implantation was performed in the Nuclear Science and Technology Development Center, in National Tsing Hua University, Taiwan. The chamber pressure during implantation was kept at 10^{-6} Torr. The implantation was carried out at room temperature. The films were irradiated using nitrogen ions (0.3 MeV) with a dose varying from 10^{13}, 10^{14} to 10^{15} ions/cm^2. It is known that violent collisions are present at the end of ions trajectories. Thus the energy of the ions was so chosen that the collision cascades would take place at and near the interface. The crystal quality of the film was investigated using Raman spectroscopy (Renishaw, 514 nm Argon Laser). The surface morphology of the sample was examined with field emission scanning electron microscope (SEM, Jeol JSM-6500F). Surface topographical information on the samples was obtained using atomic force microscopy (AFM). The interfacial morphology and elemental depth profile of the films were examined using secondary ion mass spectroscopy (SIMS, Cameca). Stress measurements were performed with surface stress induced optical deflection setup. The stress in the film was then calculated using Stoney equation [7].

A semi-quantitative approach to measure the adhesion of thin hard coating to its underlying substrate is generally achieved by using a micro scratch tester [17–19]. Here a diamond indenter is drawn across the coated surface under progressive load. The load at which the spalling of the coating occurs is defined as the critical load and is proportional to the adhesive strength of the films. The present test employed a Berkovich diamond tip oriented in face forward mode. The procedure of the scratch test is (i) the pre-scan test in which initial surface profile for scratch test was performed by moving the tip under a very small load (0.1 nN) for 60 μm followed by (ii) ramping load scratch test in which load is linearly increased from (0.1 mN to 80 mN), as the tip moved 300 μm long (from 60 μm to 360 μm) with a scratch rate of 10 μm/s and finally (iii) post scratch test in which the tip moved further for 60 μm with 0.1 mN. During the scratch test the load and penetration depth were recorded. The morphology of the scratch profile was examined by using the scan tip again with 0.1 mN load after the scratch test.

3. Results and discussion

Fig. 1 shows AFM images of the surface of the UNCD films. Diamond grains are found to be roundish-shaped. The average surface roughness (R_a) of the as-grown film measured by AFM is approximately 21 nm. The average surface roughness changes to 12 nm for the dose of 1×10^{14} ions/cm^2. With further increase in the dose to 1×10^{15} ions/cm^2, R_a changes to 19 nm. It is similar to what others have observed [20].

Raman spectra of unimplanted and ion implanted, taken at visible wavelength (514 nm) are shown in Fig. 2. There are four major peaks observed at around 1150 cm^{-1}(ν_1), 1350 cm^{-1} (D), 1480 cm^{-1}(ν_3) and 1580 cm^{-1} (G), which are assigned as graphite like sp^2 bonding (D and G) and transpolyacetylene (ν_1 and ν_3) [21,22]. The broad peak in UNCD at 1330 cm^{-1} could be due to D band type stretching in the grain boundaries. In disordered sp^2 bonded carbon, D band stretching arises from breathing mode in small aromatic clusters. There are two more peaks observed in our UNCD films at around 1190 cm^{-1} and 1550 cm^{-1}. These peaks are observed in UNCD films deposited at low temperature (as the one used in this experiment). The sharp peak at 1332 cm^{-1} is usually not observable for UNCD films as the Raman signal is much more sensitive to sp^2 bonded carbon than to sp^3 bonded carbon. The formation of transpolyacetylene further suppresses the intensity of this peak. Such phenomenon is in accordance with previously reported results [23].

Generally, the D peak broadens after ion implantation, which can be attributed to the increase in defects in the films. After nitrogen ion implantation, the overall Raman scattering intensity of the UNCD films reduces with increasing dose. At a low dose no disappearance phenomenon of Raman bands was observed (Fig. 2 (b) and (c)). But at higher dose (10^{15} ions/cm^2) the band around 1550 cm^{-1} shifts to around 1530 cm^{-1} (Fig. 2(d)). This may due

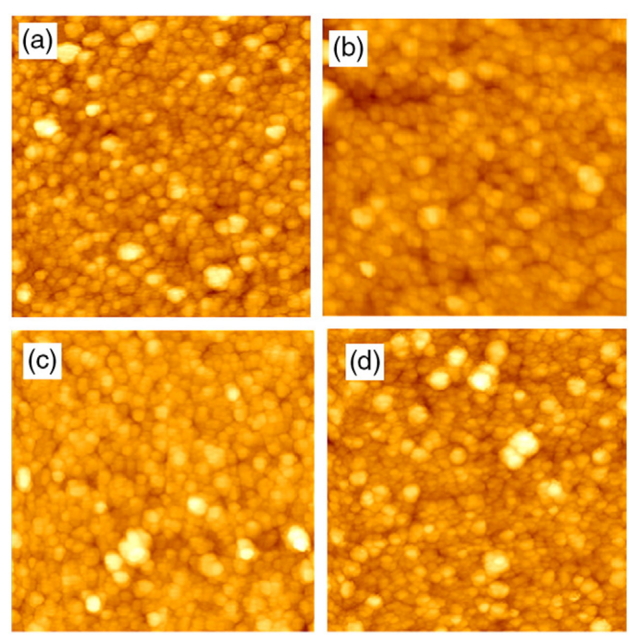

Fig. 1. AFM images of the surface of UNCD films: (a) as deposited, (b) implantation with 1×10^{13} ions/cm^2, (c) implantation with 1×10^{14} ions/cm^2 and (d) implantation with 1×10^{15} ions/cm^2.

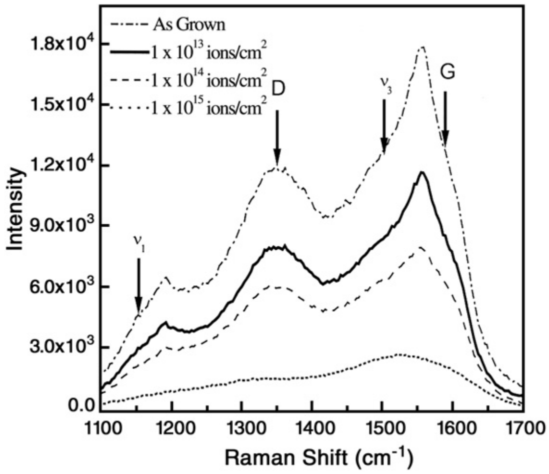

Fig. 2. Raman Spectra of UNCD films grown for 3 h: (a) unimplanted UNCD, (b) nitrogen ion implanted with 0.3 MeV and dose 1×10^{13} ions/cm^2, (c) nitrogen ion implanted with 0.3 MeV and dose 1×10^{14} ions/cm^2 and (d) nitrogen ion implanted with 0.3 MeV and dose 1×10^{15} ions/cm^2.

to the increase in amorphous carbon in the film with increasing dose. The intensity of peak related to transpolyacetylene was also found to decrease after ion implantation. Even the broad band around 1350 cm^{-1}, clearly visible in earlier doses (10^{13} and 10^{14} ions/cm^2) was not visible for 10^{15} ions/cm^2. All this indicates that large defects have been created in the UNCD film.

The stress in the film was calculated by measuring the radius of curvature of the substrate and the film. It was observed that the as-grown UNCD film has a compressive stress of 2.33 GPa. With ion implantation dose varying from 10^{13}–10^{14} ions/cm^2, the stress changes to tensile stress (4.08 GPa for 10^{13}ions/cm^2 and 0.1812 GPa for 10^{14} ions/cm^2). With further higher dose (10^{15} ions/cm^2) it shows the compressive stress (2.04 GPa). With a very small grain (about 5–10 nm) and surrounded grain boundary containing sp^2, a slight change in the composition in the grain boundary could create variation in the stress. Especially with ion implantation, the implanted ions are mostly residing in the grain boundary region (if they remain in the film instead of penetrating). The change in the composition of grain boundary is feasible. This change will be reflected in the variation of stress [24]. It was interesting to study the variation of stress on the adhesion of the film to the substrate. So the scratch test was carried out.

Fig. 3(a) represents the typical sliding wear tracks on UNCD films that resulted from nano-scratching testing procedures. It shows the critical point where the UNCD starts delaminating from the Si substrate. Fig. 3(b) shows the penetration profiles of ramping load nano-scratch surface for UNCD films grown on Si and implanted with different doses (10^{13}–10^{15} ions/cm^2) for 0.3 MeV where the surface penetration is plotted as a function of the applied load. During the nano-scratch testing the intender tip gradually penetrates into the film. The profile suddenly drops when UNCD delaminates from the Si substrate. The corresponding load at which the above phenomena happen is termed as the critical load.

The variation of critical load as a function of ion dose is given in Table 1. It can be seen that the critical load increases

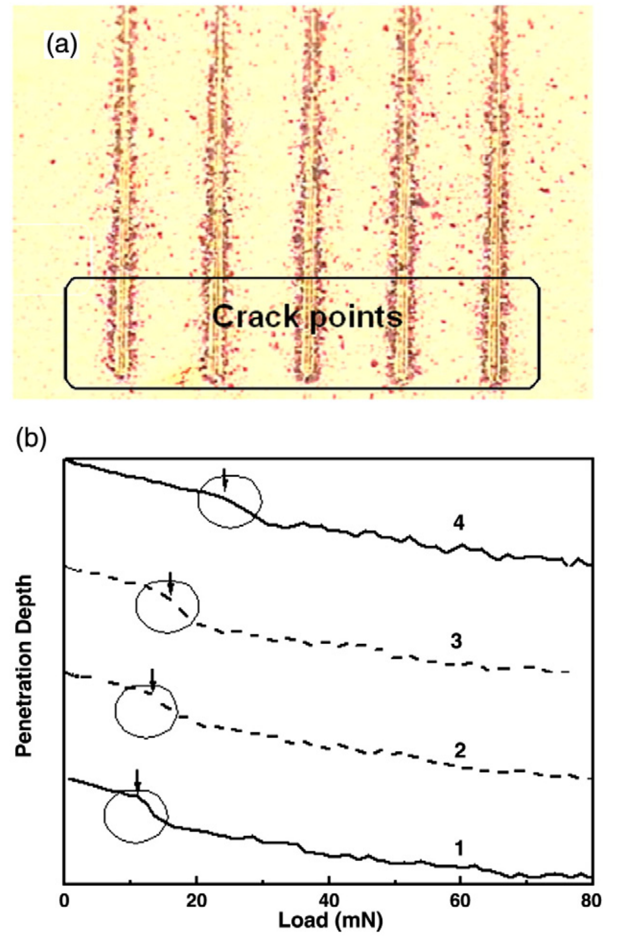

Fig. 3. (a) The micrograph showing a typical damaged image after nanointender tip scratching of UNCD films grown on silicon substrate and (b) the penetration depth curves of the nano-indenter tip scratching along the UNCD film. Inset (1) Penetration depth curve for unimplanted UNCD, (2) Penetration depth curve for UNCD with 0.3 MeV, and dose 1×10^{13} ions/cm^2 (3) Penetration depth curve for UNCD with 0.3 MeV, and dose 1×10^{14} ions/cm^2 (4) Penetration depth curve for UNCD with 0.3 MeV, and dose 1×10^{15} ions/cm^2.

with increase in dose. It means that the UNCD film is getting more adhered to the silicon substrate due to ion implantation. The measure of adhesion is the presence of thermodynamically stable interface layer.

The TRIM calculation shows that 0.3 MeV Nitrogen ion used in the present study shows a high electronic energy loss of 97 eV/Å and low nuclear energy losses of 3 eV/Å. The projected range is around 347 nm. It is almost the same as the thickness of the film. As the end of the projected range is approached, the defect density increases. As a result the atoms of the substrate and the coatings are dislodged from their respective positions, and

Table 1
The critical load in nano-scratching measurements for UNCD films grown on Silicon substrates before and after ion implantation with different doses

Samples	Critical load (mN)
Un irradiated	10.9
300 keV, 1×10^{13}	13.6
300 keV, 1×10^{14}	15.76
300 keV, 1×10^{15}	23.81

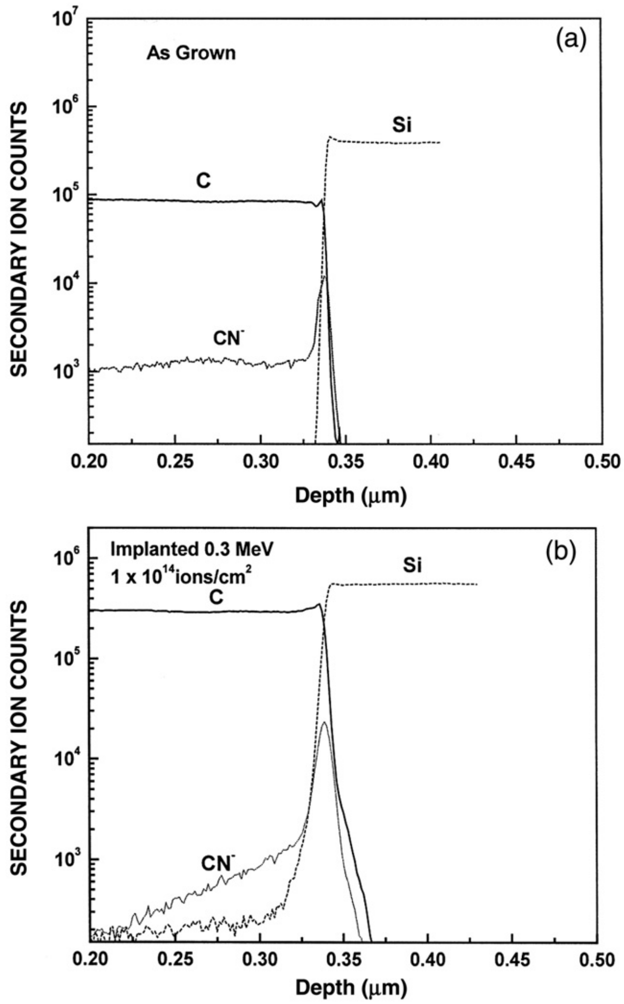

Fig. 4. SIMS spectra of (a) as-grown UNCD film and (b) UNCD film implanted with 0.3 MeV and 1×10^{15} ions/cm^2.

gain mobility due to nuclear energy relaxation of the subsequent ions. Furthermore to confirm this we examined the elemental depth profile using SIMS. Fig. 4(a) shows the SIMS spectra of as-grown UNCD film on silicon. It can be clearly seen that the carbon (solid line) and silicon (short dash) profiles drop sharply across the interface. Interestingly CN^- ions (short dots) have been observed in our as-grown UNCD films. The occurrence of CN^- ions in as-grown films is really intriguing. The origin of such high count is still under investigation. Fig. 4(b) shows SIMS spectra of implanted (0.3 MeV, 1×10^{14} ions/cm^2) film. It shows outward diffusion of Si species towards the UNCD layer and carbon species towards the substrate. The CN^- ion count is also increased substantially. All this could indicate redistribution of chemical bonds between the atoms of the films and the substrate has taken place and created an interlayer. This interlayer being chemically and thermodynamically stable has improved the adhesion of the film to the substrate.

4. Conclusion

Ultra-nanocrystalline diamond films have been implanted with nitrogen ions with energy 0.3 MeV with dose varying from 10^{13}–10^{15} ions/cm^2. The adhesion strength of UNCD films to Silicon substrate is found to increase with increase in dose. It is also observed that the stress measured varied considerably from as deposited film to ion implanted films. This may be due to the small size of grains in UNCD films, which cannot accommodate the implanted ions. Therefore, most of the implanted ions will be located in the grain boundary region (if they remain in the film instead of penetrating). Such a process can alter the stress situation in the film. But the variation of stress has shown no dominant impact in these experiments. The improvement of adhesion instead is dominated by ion induced processes at the interface. The possible mechanism behind the improvement of adhesive strength is an interfacial structure through interdiffusion between film and substrate formed due to ion implantation.

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