Structural and mechanical properties of Al–C–N films deposited at room temperature by plasma focus device

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The Al–C–N films are deposited on Si substrates by using a dense plasma focus (DPF) device with aluminum fitted central electrode (anode) and by operating the device with CH_4/N_2 gas admixture ratio of 1:1. XRD results verify the crystalline AlN (111) and Al_3CON (110) phase formation of the films deposited using multiple shots. The elemental compositions as well as chemical states of the deposited Al–C–N films are studied using XPS analysis, which affirm Al–N, C–C, and C–N bonding. The FESEM analysis reveals that the deposited films are composed of nanoparticles and nanoparticle agglomerates. The size of the agglomerates increases at a higher number of focus deposition shots for multiple shot depositions. Nanoindentation results reveal the variation in mechanical properties (nanohardness and elastic modulus) of Al–C–N films deposited with multiple shots. The highest values of nanohardness and elastic modulus are found to be about 11 and 185 GPa, respectively, for the film deposited with 30 focus deposition shots. The mechanical properties of the films deposited using multiple shots are related to the Al content and C–N bonding.

Keywords: dense plasma focus, XPS, field emission scanning electron microscope, elastic modulus

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1. Introduction

Various research groups have been working on synthesis/deposition of carbon nitride (CN_x) films for the last two decades, because of the prediction of extremely hard crystalline β-C_3N_4 solid by Liu and Cohen.[1,2] The suggestion that the hypothetical β-C_3N_4 has bulk modulus and hardness values comparable to diamond made it more interesting for researchers. After all the efforts made to synthesize the predicted crystalline β-C_3N_4, it is not clearly achieved though. Nevertheless, the amorphous carbon nitride (a-CN_x) films have been prepared with appreciably high mechanical properties. The carbon nitride (CN_x) films are a promising candidate in the area of wear protection and corrosion resistance due to their excellent properties such as high hardness, low residual stress, low coefficient of friction, and chemical inertness.[3] The superior properties on semiconductor, optoelectronics, and piezoelectric effect of AlN thin films makes it a promising candidate for applications in optoelectronics and microelectronics.[4] Consequently, Al–C–N films have received increasing attention in recent years, because they are expected to incorporate the wide band-gap, high heat conduction coefficient, high thermal and chemical stability of AlN films and the high hardness of CN_x.[5] Various techniques, such as magnetron sputtering,[5–10] implantation of nitrogen, carbon ions into aluminium,[11] and so on, are used to prepare the Al–C–N films.

One of the key features of the dense plasma focus (DPF) device is that it is simple to operate and costs less compared to other deposition techniques. The self-generated magnetic field compresses the plasma in the DPF device up to very high densities (10^{25}–10^{26} m^{-3}) and high temperatures (1–2 keV) in a short duration (10^{-7} s).[12] The highly energetic ions and relativistic electrons originate from the pinched plasma column as the plasma disrupts due to instabilities during the radial collapse phase of the DPF. These ions and electron beams have been utilized by various workers for thin film deposition and surface modification.[13–20] Recently, we reported the synthesis of Al/a-C nanocomposite thin films on silicon and a-CN_x:H films on SS-304 substrates kept at room temperature using DPF.[21,22]

In this report the deposition of Al–C–N films on silicon substrates at room temperature is carried out by using the DPF device. The DPF is a prospective hybrid deposition technique which is being used to deposit composite thin films at room temperature. It does not need extra substrate heating because the samples are heated during energetic ion beam treatment. The DPF not only possesses the interesting feature such as high deposition rate, but it also operates at very low working gas pressure. The processing of deposited film by the highly energetic ions beams generated with the DPF device results in the nanostructured Al–C–N deposition.

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2. Experimental setup

The Mather type plasma focus device designated as United Nation University/International Center for Theoretical Physics Plasma Focus Facility (UNU/ICTP PFF) has been used to deposit Al–C–N films on Si substrates. A single Maxwell (30 μF, 15 kV) fast discharge capacitor was used to energize the 3.3 kJ UNU-ICTP PFF. The set-up for the deposition of Al–C–N film using the plasma focus device is shown in Fig. 1. The dense plasma focus device is explained in detail elsewhere.[23] In this study, to deposit Al–C–N films we placed solid aluminium as an insert at the top of the engraved central electrode. The two basic electrical diagnostics tools, i.e., a high voltage probe and a Rogowski coil, were used to check the degree of focusing in the DPF device. The efficiency of the pinched plasma column was measured by the intense voltage peak in the voltage probe signal and a sharp current dip in the Rogowski coil signal. Different filling gas pressures with a CH_4/N_2 ratio of 1:1 were tried with Al fitted top to check the consistency of focusing/pinching degree of plasma. The entire deposition was carried out at a gas pressure of 1.5 mbar at which consistently good focusing was achieved. The silicon substrates were positioned at a distance of 10 cm along the anode axis above the anode tip during the whole deposition process. The capacitor was charged up to 14 kV during the entire deposition process. The three basic steps were taken to clean silicon wafers by rinsing first in acetone for 10 minutes. After that the wafers were rinsed in ethanol and de-ionized water for 10 minutes each before deposition. The rotary vane pump was employed to evacuate the chamber up to 10^{-2} mbar.

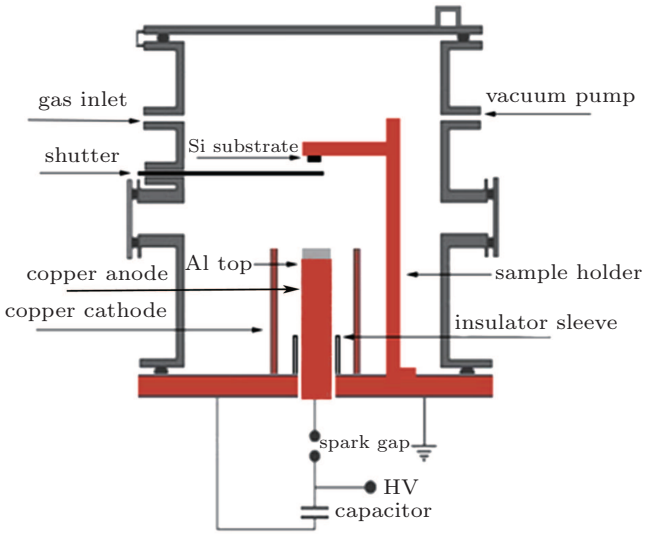


Fig. 1. (color online) Schematic diagram of dense plasma focus device.

The structural properties of the deposited composite films were studied using SIEMENS D5005 x-ray diffractometer (XRD) operated at 40 kV, 40 mA using CuK_α ($\lambda = 1.54$ Å) radiation source and the thermo scientific theta probe x-ray photoelectron spectroscopy (XPS). The surface morphology of the deposited films was studied by [Jeol JSM-6700F] field emission scanning electron microscope (FESEM) operated at 5 kV. The mechanical properties of the deposited Al–C–N films were studied by using Nano Indenter®XP (MTS system, TN, USA).

3. Results and discussion

The nucleation and growth of Al–C–N films using a plasma focus device can be understood as follows. The plasma is compressed/pinched above the central electrode by the self-generated magnetic field during the final focus phase. This plasma column consists of molecules, ions (such as carbon, hydrogen, and nitrogen), and electrons. At this instance the micro instabilities such as sausage instabilities ($m = 0$) are seen to set in the plasma column, which in turn enhances the locally induced electric field. Thus the plasma disrupts and the ions and electrons are accelerated in the opposite directions.[24] The energetic ion beams are accelerated towards the substrate (Si) while the relativistic electron beams move towards the target (Al). The highly energetic ion beams interact with the Si substrate surface resulting in the rapid increase in the substrate temperature,[25] causing higher heating in the surface of the silicon for *a* very short time duration, along with the deposition of C–N. The relativistic electron beams at the same time interacts with the anode top ablating the Al which then may or may not react with the carbon and nitrogen ions of the background gas and deposit on a Si substrate forming a Al–C–N film. The process explained above takes place during the first (single) focus shot. The deposition of Al–C–N films with multiple shot deposition results in deposition of the next layer of the film along with the processing of the previously deposited film. We utilized multiple shots (10, 20, and 30) to deposit Al–C–N films and studied the effect of focus shots on the structural, morphological, and mechanical properties.

3.1. XRD analysis

The XRD analyses of the films deposited with multiple shots on silicon substrates are shown in Fig. 2. The XRD pattern of the films deposited with 10 focus shots reveals the nucleation of crystalline AlN (111) plane. The increase in the number of focus shots for multiple shot deposition shows intensity of this phase increases. The energetic processing of the films deposited at higher (20 and 30) focus shots results in increased thickness of the film, which in turn increases intensity of AlN (111) plane.[21] A very weakly crystalline (110) phase of Al_3CON appears for 20 and 30 focus deposition shots. The unexposed silicon reveals only (311) diffraction plane, whereas the samples exposed to multiple shots show the polycrystalline Si pattern. The quenching effect (a rapid increase in temperature followed by fast cooling) produced at the sub-

strate surface due to energetic ion beams bombardment may result in the polycrystalline structure of silicon substrate.[25,26]

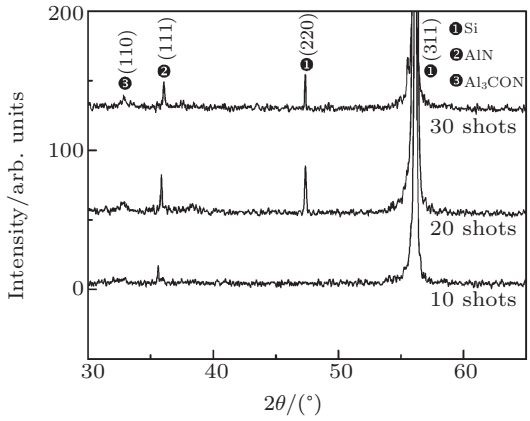


Fig. 2. XRD analysis of the films deposited using multiple shots.

3.2. XPS analysis

The XPS analyses were carried out to study the elemental concentrations as well as the chemical analysis of the films deposited with multiple shots. The surface elemental composition in atomic percentage of all the films deposited with multiple shots is given in Table 1. The XPS results show a little variation in the atomic percentage of Al, C, and N, which is associated to the shot-to-shot variation in the degree of focusing in the plasma focus device when operated with methane gas.[27] Interestingly, the Al does not react completely with the nitrogen or carbon and is present in the metallic form at the surface. When the samples are exposed to the atmosphere the metallic aluminium at the surface of deposited films reacts with oxygen. Hence, a considerable amount of oxygen is present in the deposited films.

Table 1. Elements at the surface of the films along with their atomic percentage.

No. of shots	Aluminium	Carbon	Nitrogen	Oxygen
10	10.32	55.06	7.15	27.47
20	11.74	50.65	7.17	30.44
30	9.67	56.34	7.79	26.21

The high-resolution XPS spectra of the C 1s peak of the films deposited with multiple shots are shown in Fig. 3. The asymmetric peak of C 1s spectra around 285 eV point towards the existence of various bonds in the deposited films. The Gaussian fitting for the film deposited with 10 focus shots to the XPS lines gives four peaks at binding energies 285, 286.3, 287.7, and 288.8 eV. The peaks at 285 and 288.8 eV belong to the C–C(sp^3)/C–H and C–O bond, respectively. The C 1s peaks at 286.3 and 287.7 eV are assigned to C(sp^3)–N and C(sp^3)–N bond in nitrogen-doped amorphous carbon films.[22,28–30] The deconvoluted XPS spectra of the films deposited with 20 focus deposition shots exhibit four peaks at 285, 285.4, 286.4, and 288.6 eV. The peaks at 285 and 288.6 eV correspond to C–C(sp^3)/C–H bonds and C–O bond, respectively, while at 285.4 eV belong to C(sp^2)–N. The peak at 286.4 eV corresponds to C(sp^3)–N. The XPS spectra of the films deposited with 30 focus deposition shots show four peaks at binding energies of 285.2, 286.4, 287.1, and 288.3 eV. The peaks at 285.2 and 288.3 eV belong to C–C(sp^3)/C–H with a possible influence of C(sp^2) bonding with N[22,28,30] and C–O bond, respectively. The peak at 286.4 and 287.1 eV is assigned to C(sp^3)–N and C(sp^3)–N bond in nitrogen-doped amorphous carbon films. Hence, the XPS spectra of C 1s peak for the films deposited with multiple shots show different bonding between C–C, C–N, and C–O. Besides, no peak is observed in the range of 281–283 eV for the samples treated with multiple shots which implies the absence of Al–C bonding.

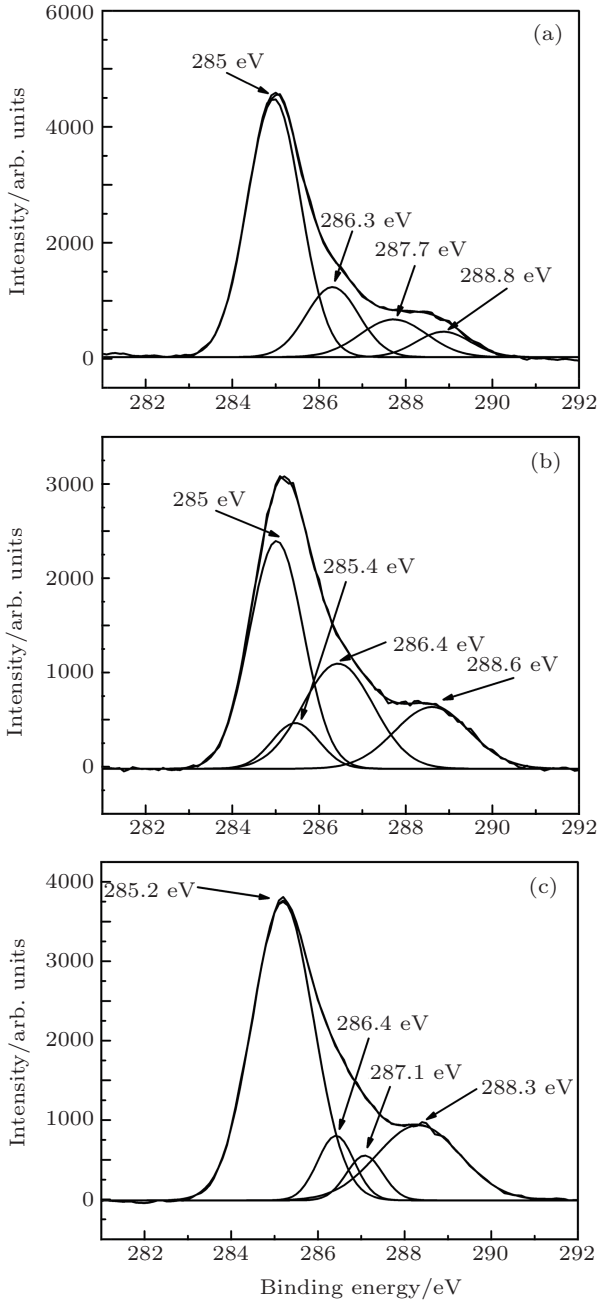


Fig. 3. The XPS spectra of the C 1s peak for the films deposited with (a) 10, (b) 20, and (c) 30 focus shots.

The high-resolution XPS spectra of the N 1s peak of the films deposited with multiple shots are shown in Fig. 4. The nitrogen spectrum of the film deposited using 10 focus shots shows three different peaks upon deconvolution. The peak at 396.6 eV is assigned to metallic nitride i-e AlN.[22] The peaks at binding energies of 398.7 and 400 eV are assigned to C(sp^3)–N and C(sp^2)–N, respectively. The samples treated with 20 focus deposition shots show three peaks at binding energies 396.5, 398.5, and 400 eV, which belong to AlN, C(sp^3)–N–, and C(sp^2)–N atoms, respectively. The XPS spectrum of the film deposited using 30 focus shots exhibit two peaks at 396.5 and 400 eV belonging to AlN and C(sp^2)–N, respectively. The broad peak at 400 eV may contain the C(sp^3)–N bond.

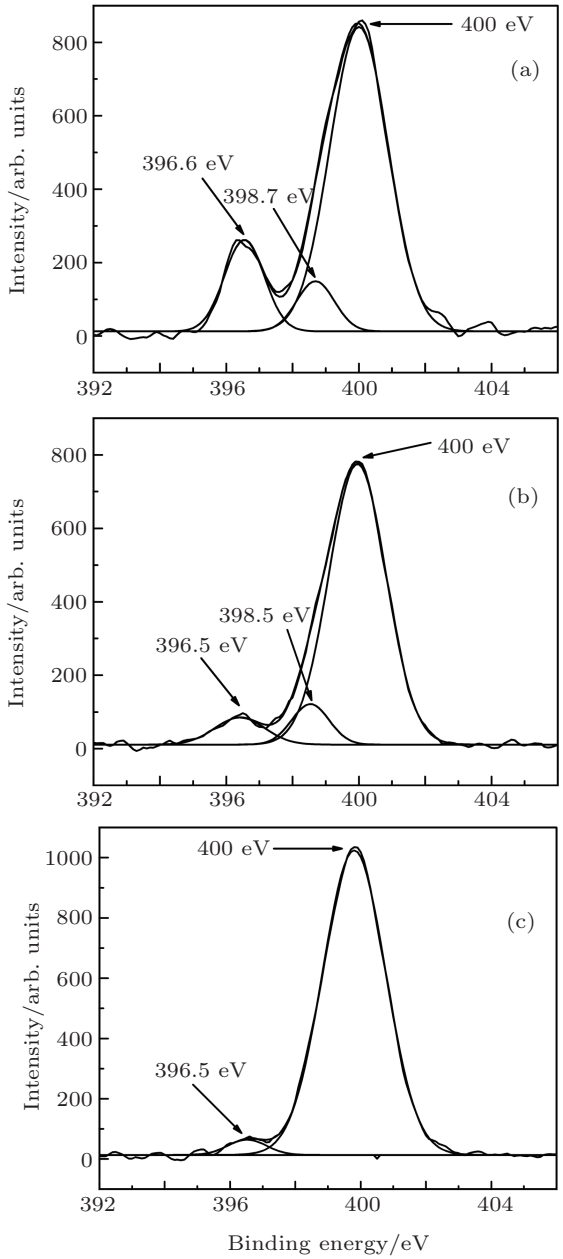


Fig. 4. The XPS spectra of the N 1s peak for the films deposited with (a) 10, (b) 20, and (c) 30 focus shots.

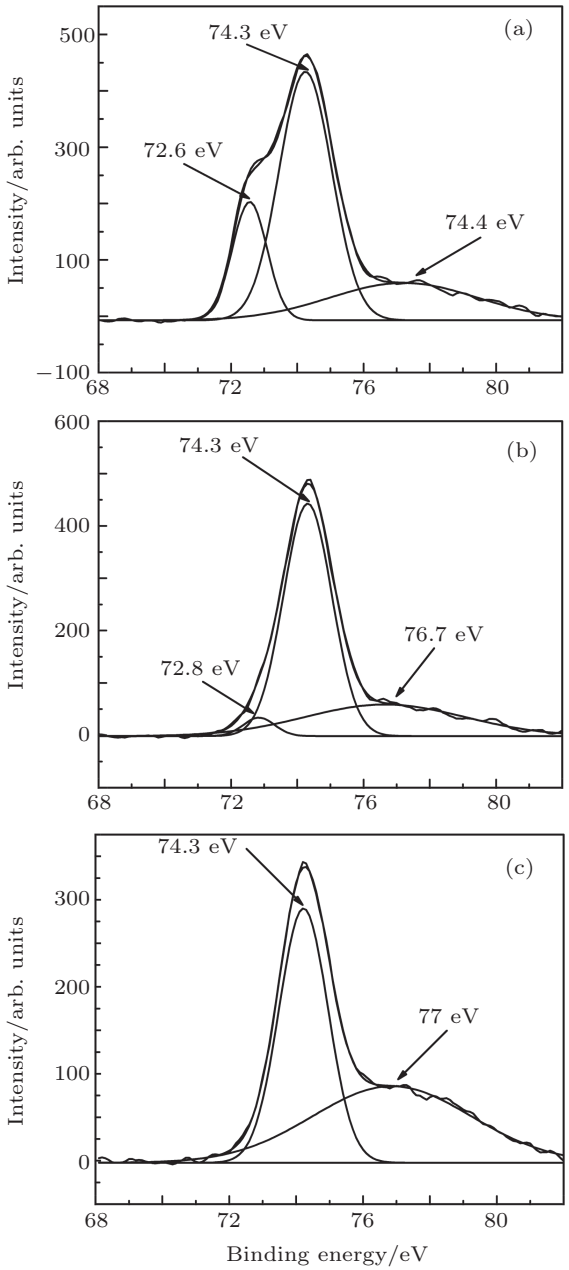


Fig. 5. The XPS spectra of the Al 2p peak for the films deposited with (a) 10, (b) 20, and (c) 30 focus shots.

The Al spectrum of the deposited film with 10 focus deposition shots exhibits three different peaks upon deconvolution as shown in Fig. 5. The peak at 72.6 eV belongs to metallic aluminium present at the surface of the film. The peaks appearing at 74.3 and 77.4 eV are attributed to AlN and Al_2O_3 present at the surface. The samples treated with 20 focus deposition shots show three peaks at 72.8, 74.3, and 76.7 eV, which belong to metallic Al, Al–N bonding (AlN), and AlO(OH) bonding respectively. The deconvoluted spectrum of the film deposited using 30 focus deposition shots show two peaks at binding energies 74.3 and 77 eV belonging to Al–N bonding and Al_2O_3, respectively. This indicates that all the metallic aluminium present at the surface of the films gets oxidized upon exposure to atmosphere. The appearance of different C–C, C–N, and AlN bonding for the films deposited with 10, 20,

and 30 focus deposition shots may be related to the multilayers structure present in the films as shown later in FESEM images which is due to the multiple shot deposition process as well as energetic processing of the films.[13]

3.3. Surface morphology

The FESEM analyses (Fig. 6) were carried out to study the surface morphologies of the films deposited using multiple focus shots. All the deposited films by multiple shots exhibit the smooth surface morphology. The film deposited with 10 focus deposition shots reveals the dense film consisting of nanoparticles. The films deposited with multiple shots show the presence of round shaped nano-sized particles at the surfaces which are indicative of the amorphous carbon present at the surface.[21,22] The films deposited with 20 and 30 focus shots show agglomeration of the nanoparticles at the surface. The agglomerates enlarge as the ion energies increase at higher focus shot and a flower-like texture appears. The large size of agglomerates at 20 and 30 focus shots are a consequence of an increase in the ion energy and ion flux.[21] The FESEM micrograph of the films deposited using 20 focus shots show multilayers composed of nanoparticles and their agglomerates (see Fig. 6(b)). Since the deposition is performed in multiple shots this results in multilayer formation.[13] Besides, the morphology of the films is composed of nanoparticles and nanoparticle agglomerates increase surface-to-volume ratio, which causes oxidation of Al present at the surface of the film[21,26] as observed earlier in the XPS results.

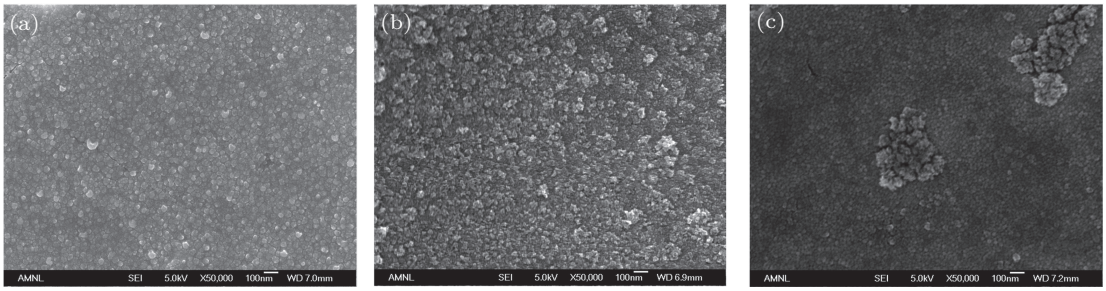


Fig. 6. Surface morphology of the films deposited with (a) 10, (b) 20, and (c) 30 focus shots.

3.4. Mechanical properties

The mechanical properties of the films deposited with multiple deposition shots (10, 20, and 30) are shown in Fig. 7. In order to avoid the surface effects on the measurement of nanohardness and elastic modulus values the results are taken at a depth of 100 nm for all deposited films. The structures and atomic concentrations of Al, C, and N of the deposited films are different owing to the treatment of the films with different ion energies and the flux at multiple shot depositions. The nanohardness and elastic modulus values are 10.2 and 159.4 GPa, respectively, for the film deposited with 10 focus shots and 7.3 and 127 GPa for the film deposited with 20 focus shots. The film deposited using 30 focus shots exhibit the highest values of the nanohardness and elastic modulus of 11 and 185 GPa, respectively. The atomic concentration of Al in all the treated samples plays a key role in terms of mechanical properties. The nanohardness and elastic modulus values are higher for the Al–C–N films deposited with 10 and 30 focus shots having low Al content and low for the films deposited using 20 focus shots having high Al content. At a higher Al content, the C–N bonding with Al decreases, which gives lower values of nanohardness and elastic modulus.[9] Moreover, the C(sp^3)–C and C(sp^3)–N bonding from XPS results are dominant for the films deposited with 10 and 30 focus deposition shots which give higher values of nanohardness and elastic modulus. Meanwhile the prominent C(sp^2)–N bonding in the film deposited using 20 focus deposition shots gives lower values of mechanical properties (nanohardness and elastic modulus). Hence, the mechanical properties of the films deposited using multiple shots depend on the Al content as well as the C(sp^3)–C, C(sp^3)–N, and C(sp^2)–N bonding.

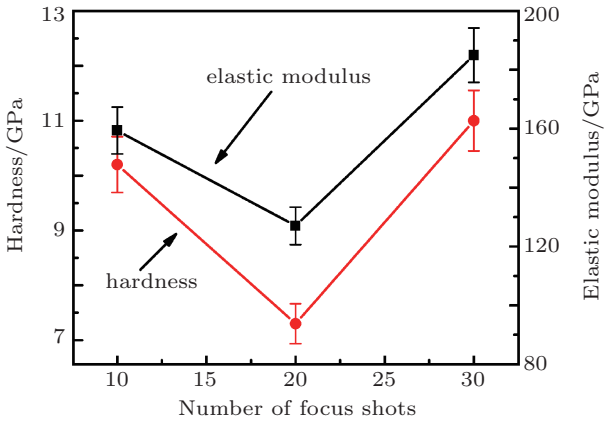


Fig. 7. (color online) Variation in nanohardness and elastic modulus of the films deposited with different number of focus shots.

4. Conclusions

The Al–C–N films have been successfully deposited by using a dense plasma focus device. XRD results authenticate the crystalline phases of AlN (111) and Al_3CON (110) for the films deposited using multiple shots. The XPS analyses validate the presence of AlN, C–C, C–N, and oxides of Al and C

at the surface of the films. The presence of metallic aluminium on the surface of all the films deposited using multiple shots implies that the aluminium plasma generated by the interaction of electron beams with Al tip, does not react completely with the reactive nitrogen and carbon ions. The metallic aluminium present at the surface gets oxidized when exposed to the atmospheric conditions. Moreover, the deposited films consist of nanoparticle and nanoparticle agglomerates which offer large surface-to-volume ratio assisting the surface oxidation. The FESEM analyses of the deposited films show an increase in agglomerates size at higher focus deposition shots. The mechanical properties of Al–C–N films are found to be dependent on the Al content in the deposited films. The highest values of hardness (11 GPa) and elastic modulus (185 GPa) are achieved for the Al–C–N film deposited using 30 focus deposition shots having the lowest Al content and dominant $C(sp^3)$–C and $C(sp^3)$–N bonding.

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