Tetrahedral amorphous carbon films prepared by magnetron sputtering and dc ion plating

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(Received 9 June 1995; accepted for publication 17 October 1995)

Highly tetrahedral, dense amorphous carbon (ta-C) films have been deposited using rf sputtering of graphite by an unbalanced magnetron with intense dc Ar-ion plating at low temperatures (<70 °C). The ratio of the argon ion flux to neutral carbon flux \( \Phi_\text{Ar}/\Phi_n \) is about 5. The film density and compressive stress are found to pass through a maximum of 2.7 g/cm\(^3\) and 16 GPa, respectively, at an ion plating energy of about 100 eV. Experiments with higher ion flux ratios of \( \Phi_\text{Ar}/\Phi_n = 10 \) show that it is possible to deposit carbon films with densities up to 3.1 g/cm\(^3\) and \( sp^3 \) contents up to 87%. Deposition of ta-C in this experiment when the energetic species is Ar appears to require a minimum stress of 14 GPa to create significant \( sp^3 \) bonding, which contrasts with the continuous increase in \( sp^3 \) content with stress when the energetic species is C ions themselves. These results are used to discuss possible deposition mechanisms. © 1996 American Institute of Physics.

I. INTRODUCTION

There has been considerable interest in highly \( sp^3 \) bonded, tetrahedral forms of amorphous carbon (ta-C) in recent years due to their remarkable physical properties. Koskinen,2 and Ishikawa, Ogawa, and Takagi,3 and Lifshitz et al.6,7 have produced ta-C films containing high fractions of \( sp^3 \) bonding using the mass selected ion-beam (MSIB) deposition method. McKenzie, Muller, and Paulethorpe6 and Fallon et al.7 have also produced highly \( sp^3 \) bonded ta-C films using a plasma beam of \( C^+ \) ions from a filtered cathodic vacuum arc (FCVA). It was found that the properties of ta-C such as density pass through a maximum as a function of \( C^+ \) ion energy in each process.

The formation of ta-C by MSIB and FCVA has generally been attributed to deposition by an energetic species, \( C^+ \). It is also possible to produce high-density a-C films by other deposition methods using energetic species,8 such as ion-assisted deposition in which energetic Ar ions bombard thermal C atoms during the deposition process. Savvides9 was able to produce diamondlike carbon by this method using an unbalanced magnetron, although his method of optical analysis is believed to overestimate the \( sp^3 \) content. Cuomo et al.10 were able to prepare a-C films with densities up to 3 g/cm\(^3\) by dual-ion-beam sputtering onto well-cooled substrates. Andre, Rossi, and Dunlop11 prepared diamondlike carbon films with densities up to 2.7 g/cm\(^3\) using a dual-ion-beam system (DIBS) and ion-beam-assisted dc magnetron (IBAM). Kleber et al.12 deposited a-C by magnetron sputtering but the films had a density of 2.0 g/cm\(^3\), which is typical of many magnetron sputtered films.

This article demonstrates that it is possible to deposit ta-C without the use of \( C^+ \) ion beams or plasma beams by using magnetron sputtering in the presence of ion plating (MS/IP). A dc-biased, unbalanced rf magnetron sputter source is operated under conditions of intense Ar-ion plating. The advantage of the magnetron sputter source is that this technique is widely established in industry and allows the deposition onto large areas with relatively high deposition rates. The use of a suitable unbalanced magnetic-field configuration places the substrate immersed in the plasma so that the growing film is bombarded by energetic Ar ions from the plasma. This MS/IP technique is quite effective and has been used by Ulrich et al.13 to deposit pure c-BN films.

The a-C films produced by MS/IP are characterized in terms of their density, \( sp^3 \) fraction, and intrinsic stress. The article also discusses possible mechanisms for the deposition of ta-C by ion plating. The data show that the deposition mechanism differs from that when the film grows from energetic \( C^+ \) ions. The growth of ta-C from energetic \( C^+ \) ions is generally believed to be described by the subplantation mechanism in which the C ions are energetic enough to enter subsurface atomic sites. In MS/IP, the energetic species is the \( Ar^+ \) ion, which acts only to bombard the growing a-C film and is not incorporated in the film. Three types of deposition processes may be of importance:

(i) displacement of C atoms by \( Ar^+ \) ions into subsurface positions (knock-on or indirect subplantation);
(ii) surface densification of the sputtered carbon atoms in the thin film by argon-ion bombardment;
(iii) conversion of \( sp^3 \) to \( sp^2 \) sites by a high local stress, which is generated by the intense argon ion plating.

These three mechanisms are expected to have different process parameters. The subplantation definitely has a threshold energy, namely the displacement energy, which for carbon lies between 25 and 35 eV. The densification process should be of importance at low collision energies (few eV) and high ion flux rates \( \Phi_i \) (compared to the flux rate of...
neutral carbon atoms $\Phi_n$). The stress-induced phase transition in the $pT$ phase diagram must show a stress threshold.

II. EXPERIMENT

The magnetron is described in detail elsewhere. In an unbalanced magnetron, the plasma extends over both the target and the substrate, so that the Ar ions provide both the sputtering flux to the graphite target and the ion plating flux on the growing film. A high flux of neutral C atoms is achieved by placing the magnets as close as possible to the graphite target. The configuration of the magnets is a critical parameter, as this determines both the neutral carbon flux $\Phi_n$ and the Ar-ion flux $\Phi_i$, thereby controlling the deposition rate and the ion plating intensity.

The substrates are sputter cleaned before deposition for 15 min and they are placed at a distance of 60 mm from the target. All films have been deposited with rf power of 200 W and rf frequency of 13.56 MHz. The argon pressure is kept constant at $1.4 \times 10^{-3}$ mbar. The substrate temperature remains below 70°C. The ion energy and ion fluxes are determined by a Faraday cup placed at the substrate position using a retarding field.

The density and $sp^3$ content were measured by electron-energy-loss spectroscopy (EELS). The plasmon spectra of the films were recorded on a 25 keV electron loss spectrometer with a typical energy resolution of 0.38 eV and an acceptance angle of 2 mrad. The spectra were corrected for the effects of multiple inelastic scattering and of the restricted acceptance angle. The density was deduced from the valence plasmon energy. Further EELS measurements were performed using a Philips CM30 transmission electron microscope (TEM) operated at 100 keV. The $sp^3$ content was derived from the intensity of the $\pi^*$ peak in the $C K$ loss spectrum, measured on a dedicated parallel EELS spectrometer on a TEM.

The stress was derived from the curvature of the Si substrates using Stoney’s equation. The thickness of the films is about 100 nm measured by ellipsometer and profilometer. The argon content was measured by Rutherford backscattering with $He^+$ ion energy of 2 MeV.

Films for optical gap measurements were prepared on quartz glass substrates, and the bias voltage was applied in the form of a rf self-bias. The Tauc gap was determined from the transmission and reflection spectra.

III. RESULTS AND DISCUSSION

A. Film properties

The analysis of the ion energy distribution and ion mass spectra show that the flux at the substrate consists mainly of neutral C atoms and Ar$^+$ ions. The mass analysis shows that the C ion flux is only about 1% of the C atom flux and therefore it does not play a significant role in the deposition process.

The energy $E_n$ of the neutral C atoms results from the energy distribution of the sputter process and amounts to a few eV. The energy of the Ar ions for zero bias voltage is given by the plasma potential of 24.2 eV and it has a rather sharp energy distribution of 7 eV. With additional bias the width of the energy distribution remains constant. The ratio $\Phi$ of the argon ion flux $\Phi_i$ to carbon neutral flux $\Phi_n$ is found to be 5.4. This means that on average each carbon atom is hit by about five argon ions while it rests on the film surface. The product $E_n\Phi_n$ is much smaller than $E_i\Phi_i$ of the argon ions and can be neglected in the energy balance during film formation.

The C atom flux was derived from the mass deposition rate. The deposition rate is 0.43 Å/s at an argon-ion energy of 24.2 eV and decreases to 0.27 Å/s for an Ar-ion energy of 130 eV. Since $\Phi_n$ and $E_n$ remains constant, the reduction in film thickness with increasing ion plating energy results partly from the densification of the material and partly from resputtering of the deposited carbon film.

The stress is seen to increase gradually and to pass through a maximum of 16 GPa at an Ar$^+$ energy of 100 eV before decreasing again at higher Ar$^+$ energies. The compressive stress variation is found to be more sharply peaked at a flux $\Phi$ of 10, reaching a value of 19 GPa at a slightly lower Ar-ion energy of 90 eV.

Figures 2 and 3 show the variation of the density and $sp^3$ content with Ar$^+$ energy for $\Phi=5.4$ and 10. As the Ar$^+$ energy increases, the density is seen to remain at a graphitic value of about 2.0 g/cm$^3$ up to 70 eV and then to increase sharply to a peak of 2.7 g/cm$^3$ at around 105 eV for $\Phi=5.4$ and to a peak of 3.1 g/cm$^3$ at 90 eV for $\Phi=10$. The density then decreases sharply at highly Ar$^+$ energies to its graphitic value. The $sp^3$ fraction behaves roughly in a similar fashion, staying at quite low $sp^3$ values and then increasing sharply for Ar$^+$ energies around 80–120 eV, before decreasing.
sharply again. The peak value of $sp^3$ fraction is 60% for $\Phi=5.4$ and 87% for $\Phi=10$.

In order to gain more information about the deposition mechanism, it is instructive to plot the density and $sp^3$ fraction against compressive stress, as shown in Figs. 4 and 5. The density variation is seen to lie on the same curve plotted versus stress for both ion flux ratios. The density is seen to remain low until the stress reaches about 13 GPa, and then increases strongly with stress. The $sp^3$ fraction also varies in a similar fashion with stress, remaining relatively constant and then increasing rapidly once the stress exceeds the threshold of 13 GPa. There is a greater scatter for the $sp^3$ data; the $sp^3$ values at low stress appear slightly higher for $\Phi=10$, but the data tend to lie in the same curve above the threshold.

This variation of density and $sp^3$ content with stress is different from that found in ta-C deposited from the FCVA, where the films are deposited by energetic C$^+$ ions themselves, where they are found to vary essentially linearly with stress.$^{6,16}$

Figure 6 shows that the $sp^3$ content varies linearly with density. A similar variation was found for ta-C from the FCVA.$^{6,16}$ A similar dependence is found because the dependence of density on $sp^3$ content is essentially a property of the material.$^{16}$ In contrast, the dependence of density and $sp^3$ content on stress is a function of the deposition process itself.

Figure 7 shows the Ar content of the $a$-C films as a function of Ar$^+$ energy as determined by Rutherford backscattering spectroscopy (RBS). The Ar content is seen to be quite low, 6%, and to decrease to a value of only 3% at an Ar$^+$ energy of 100 eV, where the film density reaches a maximum. This suggests that Ar incorporation is restricted when the ta-C density is high. Further this suggests that the main component of the stress must come from the carbon structure itself.
B. Deposition mechanism

The creation of sp$^3$ sites in ta-C prepared by energetic C$^+$ ion deposition is generally believed to arise from subplantation.\textsuperscript{4,17} The ion has sufficient energy to penetrate the surface atomic layer and enter a subsurface atomic site. There are two ways a C atom could occupy a subsurface site, either by direct penetration [Fig. 8(a)] or by incident ion displacing a surface atom into that site [Fig. 8(b)]. The subplantation also creates a large compressive stress. This process has been analyzed recently,\textsuperscript{17,18} and analytic expressions have been given for the fraction of sp$^3$ sites.

MS/IP deposition differs in that energetic Ar$^+$ ions can only displace C atoms from the surface into subsurface sites. This is analogous to the displacement process in Fig. 8(b). Subplantation by both process (a) and (b) requires the ion energy to exceed a threshold, close to the displacement energy of about 25 eV.\textsuperscript{17} The density should then increase gradually above this energy, until it begins to decrease at high ion energies, due to the annealing in a thermal spike.

A second possible process is that the Ar-ion bombardment could cause a densification of surface layers by displacing C atoms inward. In this model the densification and stress formation of the sputtered carbon atoms in the films are due to energy and momentum transfer by low-energy argon-ion plating. The knock-on collisions of the argon ions ensures that void formation is unlikely. This process is expected to be significant because each C atom is hit by on average five Ar atoms before being covered by the next layer. Densification differs from subplantation in that it does not require a threshold energy. The lack of densification at low energies however suggests that this process is relatively small in MS/IP.

The third possible process is a stress-induced transformation of sp$^2$ sites to sp$^3$ sites. McKenzie and co-workers\textsuperscript{6} attributed the generation of ta-C to a quasithermodynamic transition on a pressure/temperature phase diagram. In his model, pressure is generated by the stress in the films whereas temperature is generated by energetic carbon ions impinging on the surface of the carbon film. Takano, Harashima, and Wakatsuki,\textsuperscript{19} Endo et al.,\textsuperscript{20} and Yagi et al.\textsuperscript{21} have shock compressed graphite at room temperature. They reported a martensitic (displacive) phase transformation from sp$^2$ to sp$^3$ bonded carbon at room temperature for pressure values above 15 GPa. Scandolo et al.\textsuperscript{22} and Kitabatake\textsuperscript{23} showed by ab initio molecular-dynamic studies a pressure-induced transformation path of graphite to diamond. In the case of MS/IP ta-C we observe that the deposition process has created a very large compressive stress. This stress is larger than that found in ta-C formed by FCVA. Simulations suggest that the stress is not uniform but varies between sites.\textsuperscript{24} Since the sp$^3$ content enhances rapidly if the stress exceeds values above 14 GPa (see also Fig. 7), we propose...
that this stress causes pairs of \(sp^2\) sites to bond together to form \(sp^3\) sites. The stress in the films induces a phase transformation of \(sp^3\) to \(sp^2\) hybridized carbon. The observed threshold stress is large, about 14 GPa from Figs. 4 and 5. This stress is much larger than that given by the Berman–Simon line 1.6 GPa, which corresponds to the isothermal conversion of graphite to diamond. It seems that stress values above say 4 GPa and below 14 GPa are a necessary condition for the preparation of ta-C films, but they are not a sufficient condition for the preparation of ta-C films.

The different processes can clearly be distinguished by their different threshold energies. In the subplantation model the energy threshold is given by the displacement energy. Densification should occur if ions have a higher energy than the displacement energy. In contrast, there is no threshold in the densification model. The densification by these deposition processes plays a minor role because stress and densification do not correlate with each other and no densification is observed for Ar-ion energies below 60 eV.

In the third process, a threshold stress of about 14 GPa exists for the transformation of \(sp^2\) sites to \(sp^3\) sites. This is close to the threshold observed for shock-compressed graphite.19–21

C. Electrical properties

The Tauc gap of each of the films was found to be low, well below 1 eV, even in those films containing large \(sp^3\) contents. The optical gap is controlled by the configuration of the \(\pi\) states.25 The intense ion bombardment during deposition is likely to produce strong disordering of the \(sp^2\) sites, and to lower the optical gap.26 The lowering of the optical band gap arises from the mixing of \(\sigma\) and \(\pi\) states.

The density of electronically active defect states can be measured by electron-spin resonance (ESR). Figure 9 shows that the spin density is sizeable in MS/IP \(a-C\). The spin density is seen to be a minimum at the Ar\(^+\) energy of maximum density. The spin density is found to be less than in ta-C prepared by the FCVA,27 despite the higher disorder in the present films. This suggests that defect density is not just controlled by the intrinsic disorder.

D. Raman

The Raman spectrum of the ta-C film for \(\Phi=5.4\) is shown in Fig. 10. Generally speaking, the Raman spectra of nanocrystalline C are dominated by the features of the \(sp^2\) component because of its much larger Raman scattering. The Raman spectra are fitted by four Gaussians. The 1600 cm\(^{-1}\) G peak corresponds to the zone center Raman mode of graphite. The 1380 cm\(^{-1}\) D peak corresponds to the zone boundary mode of graphite which becomes active for finite crystallites.29 The origin of the peak at 1480 cm\(^{-1}\) is not clear.

The peak at 1170 cm\(^{-1}\) is not due to a \(sp^2\) feature. Neimanich et al.20 said that this feature is present in films with small amounts of diamond crystalline domains indicating that it could be a diamond precursor structure. They further suggested that Raman peaks around 1175 cm\(^{-1}\) are due to regions of microcrystalline diamond or amorphous diamond. Silva et al.21 attributed this peak to hexagonal diamond crys-
tallites within an amorphous carbon matrix. Wagner, Wild, and Koidl\textsuperscript{32} attributed the 1150 cm\textsuperscript{-1} peak to nanocrystalline diamond.

The MS/IP deposited films have been exposed to a microwave plasma in a H\textsubscript{2}(99%)/CH\textsubscript{4}(1%) mixture, at a substrate temperature 800 °C. These conditions are normally suitable for diamond deposition. The atomic hydrogen in the plasma causes preferential etching of amorphous and graphitic carbon structures. These conditions will even etch ta-C which has been deposited by FCVA or by a plasma beam source.\textsuperscript{33} However, the plasma does not fully etch ta-C deposited by MS/IP. This indicates that the MS/IP deposited films contain \textit{sp}\textsuperscript{3} nuclei which were not completely etched by atomic hydrogen. The treatment of such films under diamond growing conditions leads to a cauliflower appearance of growth (Fig. 11). Conclusive x-ray diffraction (XRD) measurements for the existence of diamond seeds in the films could not be performed, because the needed film thickness for XRD measurements is limited due to the high stress.

Synchrotron XRD measurements which can deal with ~100-nm-thick films are in preparation. Therefore we assume that the structure of the MS/IP deposited carbon films is given by a \textit{sp}\textsuperscript{2} matrix or net, in which \textit{sp}\textsuperscript{3} clusters are embedded. It seems that there is some, not yet identified, order in the \textit{sp}\textsuperscript{3} clusters as indicated from Raman spectra and from the diamond nucleation experiment. Such a cluster structure would explain the electronic properties (\textit{sp}\textsuperscript{2} matrix/net) and the high density. Also stress and \textit{sp}\textsuperscript{3} content are explained by the existence of such clusters.

The physical properties of the ta-C films prepared under the MS/IP conditions are completely different to those of the ta-C prepared by the MSIB technique or vacuum arc. Table I shows some physical properties for ta-C prepared by the indirect subplantation process (MS/IP) and direct subplantation process (FCVA). The different physical properties of the ta-C films have their origin in the different microstructures of the materials.

### TABLE I. Physical properties of ta-C films prepared by the MS/IP technique and FCVA (Refs. 6, 7, and 35).

<table>
<thead>
<tr>
<th>Property</th>
<th>MS/IP</th>
<th>FCVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{sp}\textsuperscript{3} content</td>
<td>87%</td>
<td>&lt;90%\textsuperscript{a}</td>
</tr>
<tr>
<td>Density</td>
<td>3.1 g/cm\textsuperscript{3}</td>
<td>~3.1 g/cm\textsuperscript{3} \textsuperscript{b}</td>
</tr>
<tr>
<td>Stress</td>
<td>&lt;19 GPa</td>
<td>&lt;11 GPa \textsuperscript{c}</td>
</tr>
<tr>
<td>Optical gap</td>
<td>\textit{c}0 eV at ( \Phi/\Phi\textsubscript{a} = 5 )</td>
<td>1.5–2.1 eV \textsuperscript{d}</td>
</tr>
<tr>
<td>Electrical resistance</td>
<td>&lt;0.25 Ω cm at ( \Phi/\Phi\textsubscript{a} = 5 )</td>
<td>&gt;10\textsuperscript{6} Ω cm\textsuperscript{d}</td>
</tr>
<tr>
<td>Raman</td>
<td>strong D peak</td>
<td>weak D peak\textsuperscript{b}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reference 34. \textsuperscript{b}Reference 6. \textsuperscript{c}Reference 36. \textsuperscript{d}References 7 and 34.

### IV. SUMMARY AND CONCLUSION

Recently, Ulrich et al.\textsuperscript{13,37} have prepared c-BN films by rf magnetron sputtering and ion plating with an c-BN content of about 93%. In both cases, the BN and the presently described C films have high fractions of \textit{sp}\textsuperscript{2} modifications. These metastable materials have higher densities than their stable \textit{sp}\textsuperscript{2} modifications, i.e., hexagonal BN and graphite. In both cases it has been shown that low-energy but intense ion bombardment with argon ions the densities of the films can be increased considerably leading to phase transition in both cases to the \textit{sp}\textsuperscript{3}-rich modifications at low temperatures.

Compressive stress in the films arises from ion peening. The compressive stress may be explained in terms of the subplantation model. However, the subplantation model does not explain the energy-dependent sharp maximum in density of the carbon films. Further the lack of densification at low ion energies suggests that (indirect) subplantation process and densification process by ion bombardment have only a small influence on the densification process.

Stress measurements reveal that \textit{sp}\textsuperscript{3} bonded carbon is predominantly deposited for stress values above 14 GPa. The existence of such a stress threshold proves that in the MS/IP a-C films exists a stress-induced transformation from \textit{sp}\textsuperscript{2}→\textit{sp}\textsuperscript{3} bonded sites. The stress threshold for the deposition of dense carbon films is much higher than the Berman–Simon line which was proposed by McKenzie and co-workers.\textsuperscript{5}

The present results indicate strong clustering of \textit{sp}\textsuperscript{3} hybridized carbon. Those \textit{sp}\textsuperscript{3} seeds are responsible for the high density in the carbon films. The electronic properties, such as optical gap and electrical conductivity of the deposited MS/IP carbon films, seem to be predominantly determined by a \textit{sp}\textsuperscript{2} matrix in which \textit{sp}\textsuperscript{3} clusters are embedded.

It follows from our experimental results that, quite generally, by low-energy ion plating at low temperatures any metastable material can be produced, if its density is higher than the density of its stable modification. This is of importance for the production of superhard coatings with C, B, and N,\textsuperscript{38} consisting of covalent bondings.

### ACKNOWLEDGMENT

The authors want to thank Professor Schmoranzer, Physics Department, University of Kaiserslautern, for most valuable support by EELS measurements.