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Effect of deposition temperature and radiofrequency discharge power on mecanical properties of nitrogenated amorphous carbon

G. LAZAR[*], V. NEDEFF, I. LAZAR, L. BIBIRE, M. STAMATE, I. CARAMAN
Bacau University, Calea Marasesti 157, 600115, Bacau, Romania

The influence of the deposition temperature and RF discharge power on the mechanical properties of nitrogenated amorphous carbon is discussed. The films are soft, porous and are easily contaminated with water vapours and other atmospheric components. The increase in deposition temperature and discharge power leads to a graphitization of the films. For films deposited by sputtering with low energy species the intrinsic mechanical stress is very high and determines the films delamination. When the precursors energy increases, the nitrogen atoms are dispersed in the aromatic structure in substitutional positions, with a higher doping efficiency and with a relief of the intrinsic stress.

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1. Introduction

Amorphous carbon (a-C) thin film research has attracted enormous interest for the last two decades due to its unique properties and possible application as cold cathodes for electron field emission [1]. However, the ability of a-C thin films to possess high intrinsic stress has been undesirable, particularly in view of microelectromechanical system applications. Excessive stress on thin films can cause adhesion problems where the film delaminates from the substrate. The internal stresses decrease and the adhesion can be improved in the cases of several important metal substrates, introducing small quantities of metal (Me) into a-C:H film matrix [2, 3]], and by deposition of an interlayer, which is gradually changed from metal to the needed composition of the Me-C:H coating [2, 3]. However, if the internal stresses in the film are large enough, then even a small external influence can induce the spalling of the layer. Compressive stress is a typical phenomenon occurring in amorphous carbon films deposited using energetic particles [4]. A simple model of this phenomenon was proposed by Davis [5].

Particularly with respect to the mechanical properties, it was found that nitrogen incorporation results in a substantial reduction of the compressive internal stress of the films. The improvement in adhesion that resulted from the stress reduction has made it possible to use amorphous hydrogenated carbon–nitrogen a-C(N):H films as antireflective coatings in Ge based IR sensors.

The study of the amorphous carbon–nitrogen alloys (a-CN_x) has recently received considerable attention since it has been shown that they are promising candidates for a number of mechanical and electronic applications, for example, as protective coatings for magnetic disks or as electronic materials in cold cathode displays. Different techniques have been successfully applied to deposit different carbon nitride phases: among them magnetron sputtering. The material greatly varies in its properties depending on the deposition method, nitrogen content or deposition temperature. The microstructure and the resulting properties of a-CN films have been widely studied, although there still exist several unanswered questions regarding how the process of growth influences the resulting structure. One of the key factors in determining the structure of amorphous carbon is the hybridisation state of the atoms that form the amorphous network. However, the detailed mechanism of the nitrogen incorporation caused by the deposition conditions during growth is not fully understood. The RF power can strongly affect the ion flux on the substrate and reactivity of the discharge plasma, as well as the flux of neutral particles (C, C2, CN, etc.) towards the substrate. In this case, the substrate temperature is a key factor because of the chemical sputtering processes from the surface of the growing film, limiting the nitrogen incorporation in the amorphous carbon films.

In this paper we present a study on the effect of the substrate temperature T_S and RF power on mechanical properties modification of a-CN films deposited by rf magnetron sputtering.

2. Experimental details

The amorphous carbon nitride films, of approximately 1 µm thick, were prepared by RFMS using pure nitrogen as sputtering gas and a 7.5 cm diameter graphite target. Prior deposition, the total base pressure was lower than 10^{-7} Torr and was maintained at 15 mTorr for all the films during growth. The target-sample holder distance was 7 cm. The samples were co-deposited onto quartz and crystalline silicon substrates for each specific characterisation technique.

Three different substrate temperatures equal to 150, 300 and 450°C were used. For each temperature, three types of films were deposited at RF power equal to 50, 150 and 300 W, corresponding to a self-bias voltage of -470, -870 and -1250 V, respectively. These conditions led to growth rates increasing in the range of 0.4- 1.5 $Å.s^{-1}$.

Stress measurements were taken from films deposited on 6x25x0.175 mm^3 (111) c-Si bars, by measuring the curvature of the Si substrate before and after deposition of films with the profilometer DEKTAK III using Stoney equation [6]:

$$\sigma = \frac{E_s t_s^2}{6\left(1-v_s\right)t_f}\left(\frac{1}{R}-\frac{1}{R_0}\right) \qquad (1)$$

where E_s , v_s , and t_s are Young's modulus, Poisson ratio, and thickness of the substrate, respectively. The Si substrate has E_s=180 GPa, v_s=0.26, and t_s=0.175 mm. R and R_0 are the radii of curvature of the film-substrate composite and bare substrate, respectively.

3. Results and discussion

The intrinsic state and magnitude of film stress is controlled by deposition conditions as they determine film stoichiometry, chemical bonding, and mechanical properties. Substrate constraint, film modulus and coefficient of thermal expansion mismatch between film and substrate control thermal stress development on cooling from the deposition temperature. Both the intrinsic and thermal components of film stress make up the deposition film stress observed at room temperature [7]. Thus, for optimum device performance and reliability it is important to be able to control film stress on deposition.

The energy of species (ions or atoms) impinging on a growing thin film is universally observed to have a dramatic impact on the properties of the resulting material. When all of the impinging species arrive with low energy (say less than a few eV), the films have been found to be porous with a large void fraction and tensile intrinsic stress [8]. As the energy of a fraction of the impinging species reaches a few tens of eV, there is a transition to intrinsic compressive stress and a corresponding densification of the material [8]. As the impinging energy of the energetic fraction reaches a few hundred eV, the intrinsic stress is seen to decrease with increasing energy and the density of the material is found to drop slightly [9] without the formation of voids or pores.

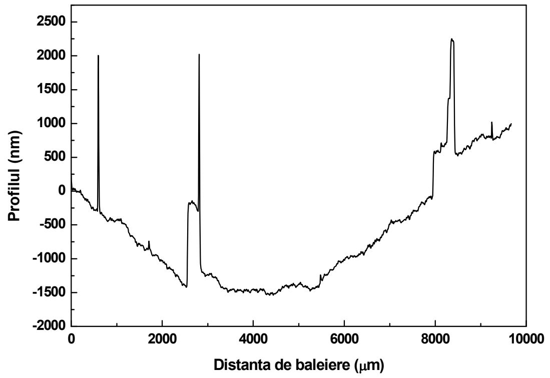

Fig.1. The surface shape of a deposited sample obtained with Dektak III profilometer

These trends with energy seem to be quite general, having been observed in a variety of materials, including microcrystalline ceramics such as aluminium nitride and titanium nitride [10] as well as amorphous materials such as amorphous carbon.

The films are soft, porous and are easily contaminated with water vapors and other atmospheric components. Films contain a large quantity of nitrogen varying from 33.5% for samples deposited at low temperatures to 15% for samples deposited at 450°C. The nitrogen proportion in films decrease also when the discharge power increase. Regarding the material structure we found that increasing the deposition temperature and discharge power the graphitization is the main effect [11-13].

The presence of the intrinsic stress is indicated by the surface shape of deposited samples, as we can see in figure 1. The curvature is obvious and the surface radius is easy to calculate.

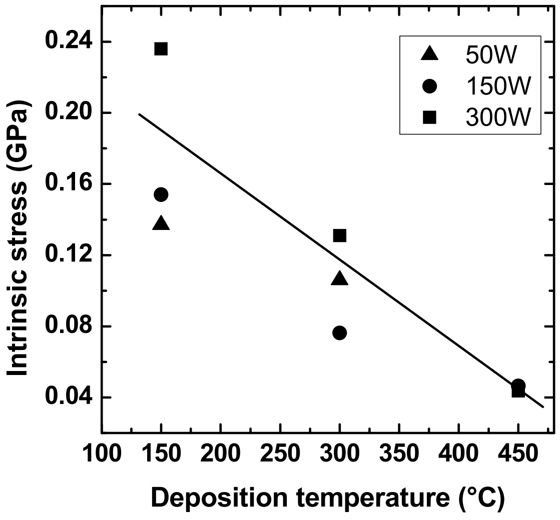

Fig.2. The intrinsic stress as a function of deposition parameters.

The results obtained for intrinsic stress measurements are shown in Fig. 2. The most important deposition parameter who determines the decrease of intrinsic stress is deposition temperature. When the deposition temperature increases, the mechanical stress almost vanishes, indicating important changes in film structure.

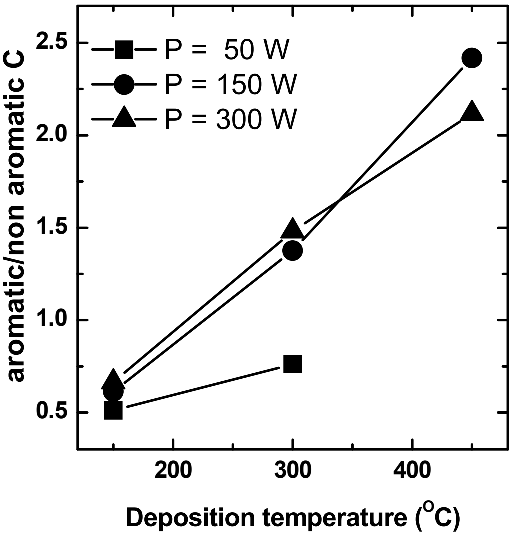

Fig.3. The rapport between the carbon atoms in aromatic structures and the carbon atoms in non-aromatic structures estimated from XPS measurements as a function of deposition temperature

In order to estimate the structure changes, we represented in Fig. 13 the rapport between the carbon atoms in aromatic structures and the carbon atoms in non-aromatic structures estimated from XPS measurements. The proportion increase rapidly when the deposition temperature increases, with a maximum value of almost 70 %. We must suppose in this case that the film is formed by graphitic nanodomains embedded in an amorphous carbon nitride matrix. These graphitic domains contain also nitrogen atoms, at the edge of the graphitic structure or as substituting atoms inside the network. In this case, the tendency of nitrogen to form pentagons instead of hexagons disturbs the network and limit the domain development. When the temperature increases, the quantity of atom carbons bonded to nitrogen in aromatic structures increases and in the same time, the nitrogen quantity decreases [13]. This implies a dispersion of nitrogen atoms in the aromatic structure, a lower influence on the matrix structure, the possibility of the size domains to increase and a relief of the mechanical stress.

4. Conclusions

The films are soft, porous and are easily contaminated with water vapors and other atmospheric components. We found that increasing the deposition temperature and discharge power the main effect which occurs is the graphitization of the films. For our films, the deposition temperature is the most important factor in decreasing the intrinsic stress. Correlated with the increase of films density, the increase of the deposition temperature induces structural changes and the intrinsic stress decreases almost to zero.

The next step is to maintain these good mechanical properties improving in the same time the optical and electrical properties.

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References

[1] C. H. P. Poa, S. R. P. Silva, R. G. Lacerda, G. A. J. Amaratunga, W. I. Milne,F. C. Marques, Appl. Phys. Lett. **86**, 232102 (2005).
[2] H. Dimigen,C.-P. Klages, Surface and Coatings Technology **49**, 543 (1991).
[3] V. Y. Kulikovsky, F. Fendrych, L. Jastrabik, D. Chvostova, L. Soukup, J. Pridal,F. Franc, Surface and Coatings Technology **102**, 81 (1998).
[4] Y. Lifshitz, Diamond Relat. Mater. **5**, 388 (1996).
[5] C. A. Davis, Thin Solid Films **226**, 30 (1993).
[6] G. G. Stoney, Proc. R. Soc. **A82**, 172 (1909).
[7] Y. Toivola, J. Thurn, R. F. Cook, G. Cibuzar,K. \ Roberts, J. Appl. Phys. **94**, 6915 (2003).
[8] D. R. McKenzie, J. Vac. Sci. Technol. B **11**, 1928 (1993).
[9] P. J. Fallon, V. S. Veerasamy, C. A. Davis, J. Robertson, G. A. J. Amaratunga, W. I. Milne,J. Koskinen, Phys. Rev. B **48**, 4777 (1993).
[10] B. K. Gan, M. M. M. Bilek, D. R. McKenzie, Y. Shi, D. A. Tompsett, M. B. Taylor,D. G. McCulloch, J. Phys.: Condens. Matter **16**, 1751 (2004).
[11] G. Lazar, M. Clin, S. Charvet, M. Therasse, C. Godet,K. Zellama, Diamond Relat. Mater. **12**, 201 (2003).
[12] G. Lazar, K. Zellama, M. Clin, C. Godet, Appl. Phys. Lett. **85**, 6176 (2004).
[13] B. Bouchet-Fabre, E. Marino, G. Lazar, K. Zellama, M. Clin, D. Ballutaud, F. Abel,C. Godet, Thin Solid Films **482**, 167 (2005).

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[*] Corresponding author: glazar21@yahoo.com