

A-C:H FILMS DEPOSITION BY SPUTTERING/CVD METHOD**G. Lazar¹***Bacău University, Calea Marășești 157, 5500, Bacău, România*

Received 2 April 2002, in final form 31 May 2002, accepted 5 June 2002

Hydrogenated amorphous carbon (a-C:H) films have been prepared by a combined magnetron sputtering-CVD deposition method in argon/methane atmosphere. The most critical process parameter determining the film properties is the ion bombardment occurring during deposition. In the presented deposition method the ion bombardment during deposition can be studied and controlled over a wide range. The effect of the deposition parameters (gas pressure, discharge power, applied bias voltage) on the deposition rate were investigated. The reactive radicals generated in the plasma were identified and monitored by optical emission spectrometry (OES).

PACS: 81.05.Gc

1 Introduction

The last two decades have seen a continued growth of our knowledge of amorphous materials and of our understanding of their properties, together with increased technological exploitation. Hydrogenated amorphous carbon (a-C:H) films have attracted considerable attention due to their wide range of technological uses, for example, as low wearing, hard, low friction coatings in engineering and medical applications [1]. Amorphous carbon has particular potential in magnetic head devices for hard disks, as a hard, low wear or anti-corrosion coating [2]. Amorphous carbon films, both hydrogenated and hydrogen free tetrahedral (a-C), have shown to be suitable for electronic applications in recent years [3]. Their electronic properties have raised interest for field emission and, more recently, for dielectric applications such as low k planarisation layers and non-volatile memories [4,5]. The potential advantage of a-C:H over other insulators lies in the higher thermal conductivity, which becomes critical as device dimensions decrease [6]. The usefulness of semiconducting amorphous carbon films for electronic applications has been enhanced by the demonstration of n-type doping by nitrogen and phosphorus or p-type doping by boron [7,8].

Due to the allotropic character of carbon which can take either sp^3 or sp^2 electronic hybridisation, the hydrogen incorporated in the material during deposition is known to control the respective proportions of the sp^3 and sp^2 carbon sites, and, consequently, the network C–C connection in the a-C:H films [9]. Such a microstructure, which plays a crucial role in the observed properties, is found to be deeply dependent on the techniques and conditions of deposition [10].

¹E-mail address: glazar@ub.ro

Hydrogenated amorphous carbon has been prepared by plasma deposition from hydrocarbon gases [6,9], sputtering [3,11], cathodic arc [12,13], ion beam methods [14] and laser vapourisation [15]. It appears that the most critical process determining the film properties is the ion bombardment occurring during deposition [16].

Sputter deposition has the advantage of coating uniformity with high deposition rate. Unbalanced magnetron sputtering can enhance ion bombardment of the substrate. In the same time, most of the species in the discharge are neutral and are difficult to control, and may result in disorder in the film.

The use of the methane gas in the sputtering plasma is rarely reported in the literature, despite of the interesting films properties. Sanchez *et al.* [17] find an increase of the sp^3 symmetric and asymmetric CH_2 IR stretching absorption peaks when the methane proportion in the plasma increases. Thus, monitoring the plasma, the deposition parameters can be controlled during the process to favour the diamond-like phase formation in the film. Mansano *et al.* [18] showed that the deposition rate of the films increases by a factor of 6 by increasing the CH_4 proportion in the sputtering plasma. FTIR characterization showed that the films deposited with CH_4 containing plasmas are much richer in sp^3 type carbon than when deposited with pure Ar plasmas.

In this work, the amorphous hydrogenated carbon deposition is presented for a combined magnetron sputtering-CVD deposition method. The method uses a RF magnetron discharge, with an applied DC bias voltage on substrate holder, using a mixture of argon with methane as discharge gas. The effect of the deposition parameters (gas pressure, discharge power, applied bias voltage) on the deposition rates were investigated.

2 Experiment

Hydrogenated amorphous carbon films were deposited by magnetron sputtering technique, using pure graphite target, 7.5 cm in radius, and 99.99 % pure Ar/ CH_4 gas mixture. The magnetron installation shown in Fig. 1.a was built in our laboratory in order to deposit thin films by DC or RF planar and circular magnetron sputtering [19–21]. 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. The energy and the flux of the ions reaching the growing film surface were varied by applying an external bias voltage (from -400 V to $+400$ V) to the substrate.

The deposition technique is a combination of a regular magnetron sputtering method and of plasma assisted chemical vapour deposition. The plasma must provide the ions for target sputtering and decompose the methane gas for a better hydrogenation of films. High flux of neutral C atoms is achieved by placing the magnets as close as possible to the graphite target. The configuration of the magnetic field is the critical parameter controlling the deposition rate and the ion plating intensity [22] and is a particular property of the magnetron.

In this work, the magnetron plasma is formed using a RF-power supply (13.56 MHz) connected to an electrode 8 (cathode) and grounded circular anode (3). The RF electrical field dissociates the methane molecules to electrons, ions and radicals and excites or ionises argon atoms. Due to their smaller masses, electrons have much greater mobility in discharge than ions. This leads to a negative feed-back between the circular anode and the cathode. The negative potential on cathode accelerates positive ions from plasma to the target what results in sputtering.

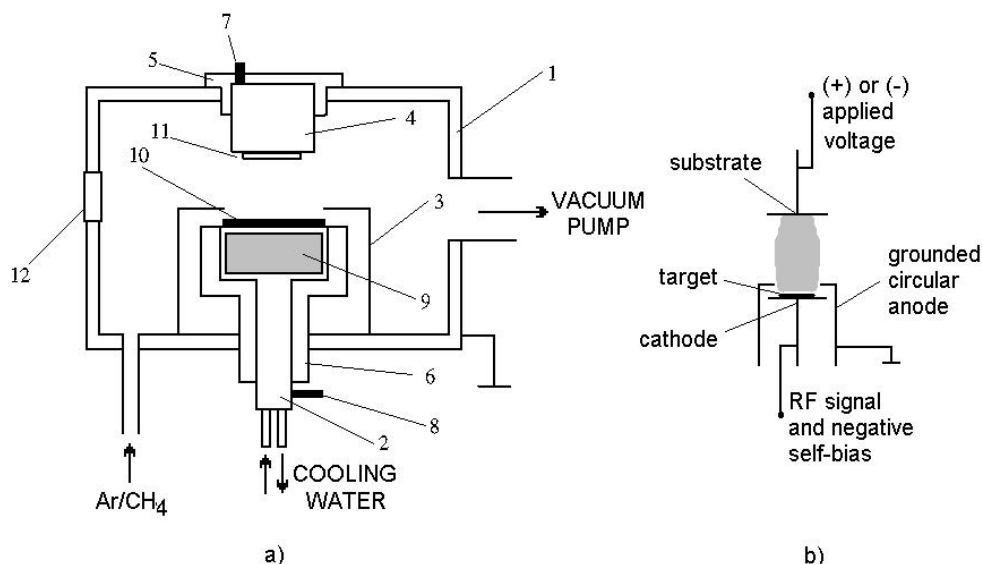


Fig. 1. a) The sputtering system: 1 - cylindrical stainless-steel chamber; 2 - cathode; 3 - circular anode; 4 - planar anode; 5,6 - isolators; 7,8 - electrodes; 9 - magnets; 10 - target; 11 - substrate; 12 - window; b) The system of electrodes and their biasing.

A stabilised DC power supply ($0 - \pm 500$ V, 240 mA) connected to an electrode 7, was used for negative or positive feed-back of the substrate, see Fig. 1.b.

Films were deposited on glass substrates at a target-to-substrate distance of 3 cm. The volumetric proportion between Ar and methane gas was maintained constant at 1/1. The total pressure was adjusted between 26 Pa (0.2 torr) and 1.3 Pa (0.01 torr). The substrate temperature during the deposition was below 100°C for all samples. The substrates were partially masked to measure the films thickness by Tolansky instruments. The growth rate of a-C:H films was measured as a function of pressure, discharge power and DC substrate bias. The reactive radicals generated in the plasma were identified and analysed by optical emission spectrometry (OES).

3 Result and discussion

The deposition rate of a-C:H films is an important parameter for evaluating the efficiency of the films deposition method and installation. The major interest of the study is to obtain larger deposition rate, without negative influence on film properties.

Generally, the films are smooth, transparent and colourless when they are deposited at pressures around 26 Pa and soft yellow when the deposition gas pressure is lowered to 1.3 Pa. For a bias voltage bellow -200 V the bombardment of the positive ions on the substrate is very intense and the colour of deposited films is modified to a non-transparent dark brown. For a positive bias voltage applied to the substrate, the electrons from plasma are accelerated, improving the discharge efficiency and the methane dissociation degree. In Fig. 2 the I-V characteristics for

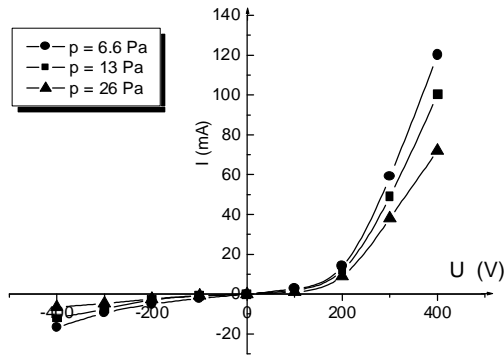


Fig. 2. The I-V characteristics for the DC applied bias voltage, for three different gas pressures.

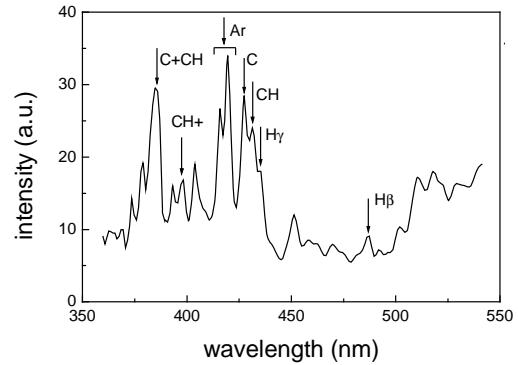


Fig. 3. Emission spectrum from discharge used for a-C:H film deposition at 2 Pa, with 0 V applied bias voltage and 70 RF power.

the DC applied voltage are presented for three different pressures. The system is acting like a diode. When the negative applied voltage increases, the current presents a slow increasing due to negative feed-back of the cathode. When the applied voltage on the substrate is positive, the accelerated electrons lead to a rapidly increase of current intensity. In the same time, the increase of the negative applied voltage led to a strong substrate bombardment. The film is back-sputtered, the deposition rate is lowered and the film properties are modified. The films obtained at an applied bias voltage of -400 V are black and present a very weak adhesion to the substrate. Optical emission spectroscopy (OES) was used to diagnose and monitor the plasma discharges generated in a $\text{CH}_4 + \text{Ar}$ gas atmosphere, used for the a-C:H deposition. This technique has proven to be an effective tool in determining the gas intermediate species participating in the reaction mechanisms. In Fig. 3, a typical emission spectrum of the CH_4/Ar discharge is shown, corresponding to a deposition gas pressure of 2 Pa, with 0 V bias voltage and 70 W RF discharge power. The most important features in the RF discharge are the Ar emission lines in the range of 415 nm to 420 nm [23]. The spectrum basically presents the emission peaks corresponding to CH (390 nm and 431 nm), H_β (486 nm), H_γ (434 nm) and C (427 nm and 392 nm) and it is an evidence of methane decomposition. The deposition is produced from both carbon species: the sputtered carbon and the methane carbon produced by decomposition. The presence of the hydrogen in the plasma and in the methane radical species leads to the formation of a high hydrogenated, sp^3 rich, polymer-like amorphous carbon film [21].

Another important parameter of the deposition installation is the dependence between gas pressure and deposition power, for a constant value of the applied RF signal. The variation of the discharge power versus gas pressure for three values of applied bias voltage is shown in Fig. 4. When the pressure increases, the discharge power decreases. This is slower in the range of 1.3 Pa to 6.6 Pa and faster in the range of 6.6 Pa to 26 Pa. Because of the electric field generated by the voltage applied between the anode and the cathode, the power increases slowly with voltage.

The variations of the deposition rate with the gas pressure for three values of the applied bias voltage and a constant RF applied signal are presented in Fig. 5. The variation of the deposition rate is similar to the variation of the discharge power (see Fig. 4) and indicates a linear increase

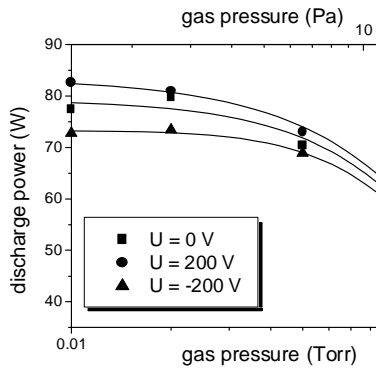


Fig. 4. The variation of discharge power with deposition gas pressure for three values of the applied bias voltage.

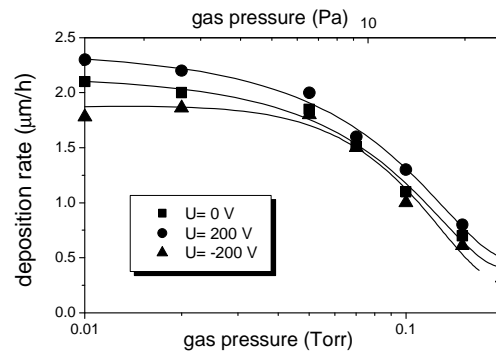


Fig. 5. The variation of deposition rate with deposition gas pressure for three values of the applied bias voltage.

of the deposition rate with the discharge power. For this method, the variation of the deposition rate with gas pressure is different from the case of the deposition from glow discharge, where the deposition rate increases when the gas pressure increases. In the sputtering process, both the free path of the deposition species and the deposition rate decrease with increasing pressure. In the glow discharge deposition, the quantities of the film components and the deposition rate increase with increasing gas pressure. According to these results, the sputtering method is more efficient for thin film deposition at lower pressures.

The main reason of increase of the deposition rate with decrease of the pressure is the decrease of the deposition power. The dependency between the deposition rate and the discharge power (see Fig. 6) reveals the proportionality between the two parameters. The increase of the deposition rate with the positive applied voltage is due to the improvement of the discharge efficiency and sputtering process.

The substrate bias voltage influences the deposition rate. The variation of the deposition rate with substrate applied bias voltage is shown in Fig. 7. When the applied bias voltage increases, the discharge power and the energy of the deposition species increase, resulting an increasing of the deposition rate. For negative applied bias voltage, there is also another reason for decreasing of the deposition rate, namely the back sputtering.

The deposition rates reported in this paper are similar to the results from pulsed laser deposition [24] or hot filament chemical vapour deposition [25]. Using the DC magnetron sputtering method, F. Richter *et al.* [26] reported values of the deposition rate about $2.5 \mu\text{m/h}$, using much greater values of the deposition power, cca 900 W. Values of the deposition rate in the range 1–2 $\mu\text{m/h}$ are also reported for RF magnetron sputtering deposition of amorphous carbon thin films, but for greatest RF powers (150 W) [18,27].

4 Conclusions

The most critical process parameter determining the amorphous carbon film properties is the ion bombardment occurring during deposition. The main advantage of the presented deposition

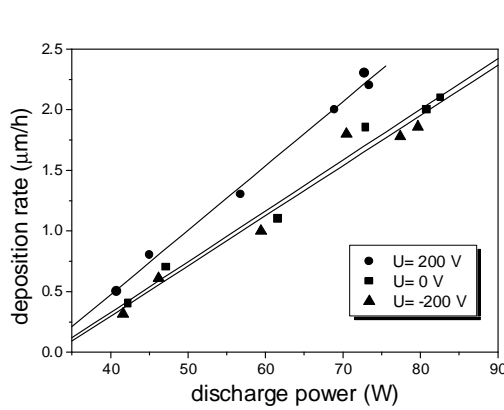


Fig. 6. The variation of deposition rate with discharge power for three values of the applied bias voltage.

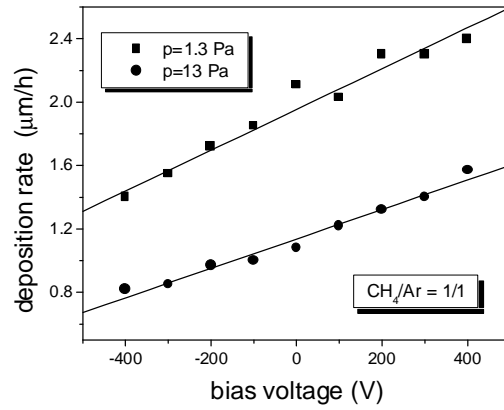


Fig. 7. The variation of deposition rate with applied bias voltage for two values of the deposition gas pressure.

method consists of the possibility to study and to control the ion bombardment in a wide range during deposition.

In this work, the deposition rate of hydrogenated amorphous carbon thin films is presented for a combination of a regular magnetron sputtering method and a plasma assisted chemical vapour deposition. The method uses a RF discharge, with an applied DC bias voltage on substrate holder. The obtained deposition rate is of the same order of magnitude as the reported results for other high technology deposition methods and it is higher than the deposition rate usually reported for RF magnetron sputtering deposition, using the same value of the discharge power. The deposition rate is influenced by the deposition gas pressure, the discharge power and the substrate applied bias voltage.

References

- [1] J. McLaughlin, B. Meenan, P. Maguire, A. Ogwu, R. Lamberton, J. F. Zhao, P. Lemoine: *Int. J. Modern Phys. B* **14** (2000) 167
- [2] M. K. Fung, K. H. Lai, H. L. Lai, C. Y. Chan, N. B. Wong, I. Bello, C. S. Lee, S. T. Lee: *Diamond Relat. Mater.* **9** (2000) 815
- [3] N. Konofaos, E. Evangelou, S. Logothetidis: *J. Appl. Phys.* **86** (1999) 4446
- [4] S. R. P. Silva, R. D. Forrest, D. A. Munindradaso, G. A. J. Amaratunga: *Diamond Relat. Mater.* **9** (2000) 1205
- [5] A. Grill: *Thin Solid Films* **356** (1999) 189
- [6] P. D. Maguire, D. P. Magill, A. A. Ogwu, J. A. McLaughlin: *Diamond Relat. Mater.* **10** (2001) 216
- [7] C. W. Chen, J. Robertson: *Carbon* **37** (1999) 839
- [8] C. H. Lee, S. K. Lim: *Appl. Phys. Lett.* **72** (1998) 106
- [9] M. Clin, M. Benlahsen, A. Zeinert, K. Zellama, C. Naud: *Thin Solid Films* **372** (2000) 60
- [10] T. Heitz, B. Drevillon, J. E. Bouree, C. Godet: *J. Non-Cryst. Solids* **227–230** (1998) 636

- [11] J. Schwan, S. Ulrich, H. Roth, H. Ehrhardt, S. R. P. Silva, J. Robertson, R. Samlenski, R. Brenn: *J. Appl. Phys.* **79** (1996) 1416
- [12] Yusuke Taki, Osamu Takai: *Thin Solid Films* **316** (1998) 45
- [13] K. B. K. Teo, S. E. Rodil, J. T. H. Tsai, A. C. Ferrari, J. Robertson, W. I. Milne: *J. Appl. Phys.* **89** (2001) 3706
- [14] R. S. Brusa, A. Somoza, H. Huck, N. Tiengo, G. P. Karwasz, A. Zecca, M. Reinoso, E. B. Halac: *Appl. Sur. Sci.* **150** (1999) 202
- [15] Z. Y. Chen, J. P. Zhao, T. Yano, T. Ooie, M. Yoneda, J. Sakakibara: *J. Appl. Phys.* **88** (2000) 2305
- [16] E. H. A. Dekempeneer, R. Jacobs, J. Smeets, J. Meneve, L. Eersels, B. Blanpain, J. Roos, D. J. Oostra: *Thin Solid Films* **217** (1992) 56
- [17] N. A. Sanchez, C. Rincon, G. Zambrano, H. Galindo, P. Prieto: *Thin Solid Films* **373** (2000) 247
- [18] R. D. Mansano, M. Massi, L. S. Zambom, P. Verdonck, P. M. Nogueira, H. S. Maciel, C. Otani: *Thin Solid Films* **373** (2000) 243
- [19] I. Lazar, I. Vascan: *Romanian Journal of Physics* **43** (1998) 333
- [20] M. Stamate, I. Vascan: *Romanian Journal of Optoelectronics* **5** (1997) 47
- [21] G. Lazar: *J. Phys.: Cond. Matter.* **13** (2001) 3011
- [22] J. Schwan, S. Ulrich, H. Roth, H. Ehrhardt, S. R. P. Silva, J. Robertson, R. Samlenski, R. Brenn: *J. Appl. Phys.* **79** (1996) 1416
- [23] L. Martinu, A. Raveh, A. Dominique, L. Bertrand, J. E. Klemberg-Sapieha, S. C. Gujrathi, M. R. Wertheimer: *Thin Solid Films* **208** (1992) 42
- [24] Z. F. Li, Z. Y. Yang, R. F. Xiao: *J. Appl. Phys.* **80** (1996) 5398
- [25] S. Bohr, R. Haubner, B. Lux: *Appl. Phys. Lett.* **68** (1996) 1075
- [26] F. Richter, K. Bewilogua, H. Kupfer, I. Muhling, B. Rau, B. Rother, D. Schumacher: *Thin Solid Films* **212** (1992) 245
- [27] A. K. M. S. Chowdhury, D. C. Cameron, M. A. Monclus: *Thin Solid Films* **355–356** (1999) 85