Journal of Optoelectronics and Advanced Materials Vol. 5, No. 3, September 2003, p. 667 - 673

NANOSTRUCTURED CARBON THIN FILMS DEPOSITION USING THERMIONIC VACUUM ARC (TVA) TECHNOLOGY

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In this paper carbon film condensation from the carbon plasma generated by a Thermionic Vacuum Arc with carbon anode is presented. The carbon film is bombarded during its deposition by energetic carbon ions with established value of directed energy. High purity, hydrogen free and nanostructure layers are obtained, the characteristic size of structures being in the order of few nanometers. Thermionic Vacuum Arc (TVA) is an externally heated cathode arc which can be established in high vacuum condition, in vapors of the anode material. It is ignited between a heated cathode surrounded by an electron focusing Whenelt cylinder and an anode carbon rod. Due to the electron bombardment anode material starts to evaporate ensuring a steady state concentration of the evaporated carbon atoms in the cathode – anode space. At further increase of the applied high voltage, a bright discharge is established in the carbon vapors. Besides the evaporated neutral atoms, on the sample are also incident energetic ions. So, the thin film is growing under the bombardment of ions of the material to be deposited. This is a major advantage in obtaining high purity thin films because the discharge is ignited in vacuum and the film is bombarded during its growing with own atoms which are ionized. The ions have a random energy superposed on a much higher directed energy towards the wall. Directed energy of ions can achieve values of the order of 500 V.The deposited C films were studied using TEM electronic microscopy with a magnification of 1.4 M and a resolution of 1.4 Å. The samples of deposited carbon film (deposited on NaCl or KCl monocristals, solved in water before TEM examination) show nanostructures films. The new system of deposition is peculiarly adequate for hydrogen free, high quality-smooth and compact-DLC film deposition. TVA easily ensures the needed high value of the energy to evaporate pure carbon. Rhomboidal structure with lattice parameters: a = 0.25221 nm, c = 4.3245 nm (ASTM pattern: 79-1473) of diamond/carbon has been obtained as evidenced from electron diffraction pattern.

(Received July 11, 2003; accepted July 31, 2003)

Keywords: Thermionic Vacuum Arc, Carbon thin film, Nanostructure

1. Introduction

Thin films production represents today not only one of the most used technology but also a continuously developing one. The progress in miniaturization of various highly integrated circuits, improvement of the superficial properties like micro hardness, friction, chemical inertness, needs more improvements concerning film quality.[1] Indeed, with the decrease of the roughness, the thickness of the thin film can be reduced under 100 Å, which means a layer nearby transparent for any wavelength.

One of the most promising thin film layers are those obtained by DLC (diamond like carbon) coating as a result of plasma-chemical processing of hydrocarbons (like methane). Usually the obtained thin films have a content of hydrogen [2].

Recently, hydrogen free thin layers of DLC were studied in order to get better quality of such films.

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The aim of this paper is to present a new, very promising technology, with a broad area of application and especially suitable for high quality carbon thin film deposition in high vacuum conditions.

This technology has been used successfully for various metal or oxide thin film deposition [3] but the most adequate application is related to nanostructured carbon film deposition. Indeed, the carbon anode is easily transformed into vapors due to electron beam bombardment, the purity of the deposited film is ensured by high vacuum condition and the compactness and smoothness due to the film growing under the high energy ion bombardment during deposition.

2. Experimental

Thermionic Vacuum Arc can be ignited in vacuum (or UHV) between a heated cathode surrounded by an electron focusing Whenelt cylinder and an anode (tungsten crucible) containing the material to be deposited. Due to the electron bombardment of the anode by the accelerated thermo-electrons from the grounded cathode towards the anode (which is at high voltage), anode material first melts and afterwards starts to evaporate ensuring a steady state concentration of the evaporated atoms in the cathode – anode space [4].

At further increase of the applied high voltage, a bright discharge is established inside of the vacuumated vessel in the vapors of the anode material. In Fig. 1 it is schematically shown the TVA electrodes arrangement. The following parameters are fully controlling the TVA: arc current I_{arc}, cathode thermoelectronic emission current, controlled by the heated cathode temperature T_c, interelectrodic distance d, angle φ between an imaginary perpendicular line on the anode and the axis of the heated cathode.

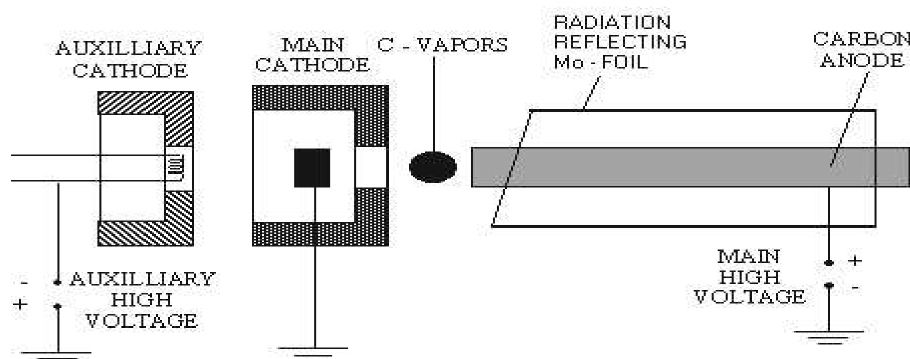

Fig. 1. Schematic view of the electrodes arrangement for carbon plasma generation (indirectly heated cathode).

The thickness of the deposited carbon films on Si wafers of the order of 100-200 nm.

During the experiments, a simple solution has been found both for cathode and anode. As cathode we used a thick filament wire with 1.5 mm diameter from thoriated tungsten and as anode we used a carbon rod of short length supported by a refractory metal wire (tungsten) with a diameter of 1.5-2 mm.

In Tabel 1 are shown the main used working parameters: the cathode filament is made by thoriated tungsten wire with 1.5 mm diameter, three times wound and heated by a current of 100 A.

During the arc running and carbon thin film deposition, the anode was continuously rotating with 6 rotation/minute and also the cathode-anode distance was adjusted each time when the arc current was decreasing more than 10%. This way, a continuous working of the TVA was ensured.

Table 1. The main working parameters used during arc using in pure carbon.

Cathode – anode size	*TVA*	*Carbon deposition*
Carbon - anode diameter: 10 mm	Current: 1.25 A	Time: 300 s
Carbon - anode length: 10 mm	Applied d.c. HV: 1.1 kV	Rate: 30 nm/s
Carbon - anode distance: 4 mm	Working pressure: $\leq 10^{-6}$ torr	Film thickness: 90 nm

Since the cathode of TVA is at earth potential and vacuum vessel also, it results that the plasma has a potential accelerating ions towards against the vacuum vessel wall. This potential is roughly equal with the cathode potential fall (see Fig. 2).

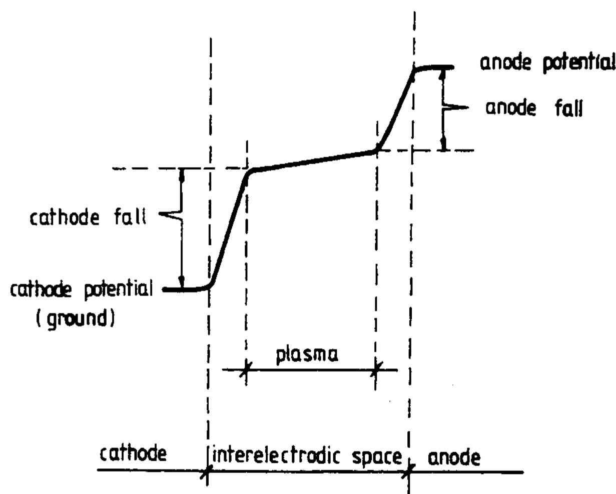

Fig. 2. Potential distribution in the cathode–anode space.

In these circumstances, besides the evaporated neutral atoms, on the sample are also incident energetic ions. So, the thin film is growing under the bombardment of ions of the material to be deposited. This is a major advantage in obtaining high purity thin films because the discharge is ignited in vacuum and the film is bombarded during its growing with own atoms which are ionized. We measured, using a special retarding potential analyzer, the energy of ions in a TVA discharge, an experimental curve being given as example in Fig. 3 [5].

The ions have a random energy superposed on a much higher directed energy towards the wall. Directed energy of ions can achieve values of the order of 250 V. Our measurements on the potential distribution inside the vacuum vessel during TVA discharge have proved a continuous plasma source decrease of this potential from the value of the potential of the to the ground potential of the vacuum vessel wall. It results that the ion energy is directly related to the potential difference between vacuum vessel potential and plasma potential i.e., cathode potential fall.

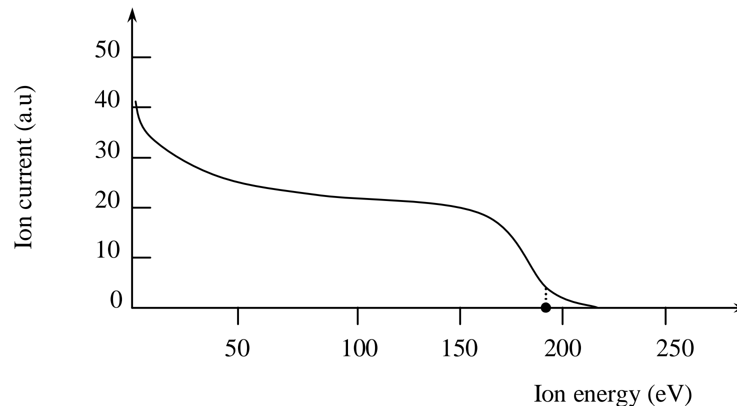

Fig. 3. Energy distribution of ions in TVA metal vapor plasma.

The ions have a random energy superposed on a much higher directed energy towards the wall. Directed energy of ions can achieve values of the order of 250 V. Our measurements on the potential distribution inside the vacuum vessel during TVA discharge have proved a continuous decrease of this potential from the value of the potential of the plasma source to the ground potential of the vacuum vessel wall. It results that the ion energy is directly related to the potential difference between vacuum vessel potential and plasma potential i.e., cathode potential fall. As a result, the ion energy of the TVA plasma can be straightforward controlled and established at needed value even during arc running. For this, it is enough to control the given cathode potential fall. We were able to establish the means to control the ion energy at a constant maintained TVA arc current. For example, a cathode fall increase is obtained using one of the below changes of TVA parameters: (1) decrease of the cathode temperature, (2) increase of angle φ, (3) increase of the interelectrodic distance d. In Fig. 4 is presented the dependence of the copper ions for a thermionic vacuum arc discharge in respect with the arc current for two values of the angle φ. Strong dependence of the ion energy on these parameters can be seen [6].

An empirical relation can be established between the cathode potential fall and the TVA arc voltage drop, the relation between these two parameters being a linear one. In most of the cases, the ratio between these two potentials is roughly 1/2 - 1/3. In Fig. 4 is given the correlation between experimentally measured values of the energy of ions and the arc voltage drop.

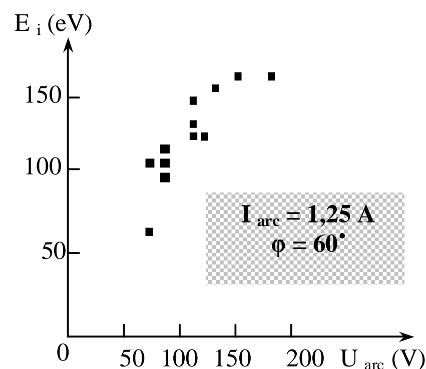

Fig. 4. Correlation of measured maximum ion energies and the arc voltage drop U_{arc} where φ defines the angle between the imaginary line perpendicular to the anode and the axis of the cathode.

These data were taken for a TVA discharge with an arc current of 1.25 A and for a value of the parameter $\varphi = 80^{\circ}$. A steadily increase of the energy of ions with the value of the arc voltage drop can be observed. Consequently, the continuously measured value of the arc voltage drop can be used as direct information on the value of the ion energy.

We shall now underline our main obtained results in using TVA technology for thin film deposition: SEM analysis of the deposited thin films have shown no droplets (droplets free deposition) and presented a compact structure of the fractured film.

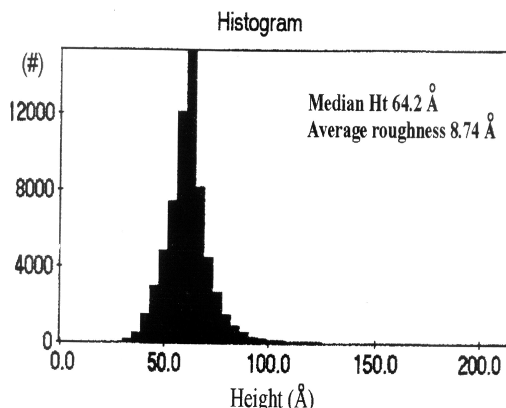

Fig. 5. Histogram of measured height distribution.

Atomic force measurements of the deposited copper film have shown very smooth surfaces. Roughness values in the order of 40 A were usual. In Fig. 5 is presented a histogram of the height distribution from which median and average roughness can be evaluated [7].

Also we measured the roughness dependence on the value of the directed ion energy, proving clear decrease of the roughness with the energy of incident ions on the depositing film (see Fig. 6).

Due to the incident energetic ions, the adherence of the thin film on the substrate increases especially in the case of plastic materials. In this case, in accordance with our results, the adherence is directly related to the value of the ion energy, increasing with the ion energy value [8].

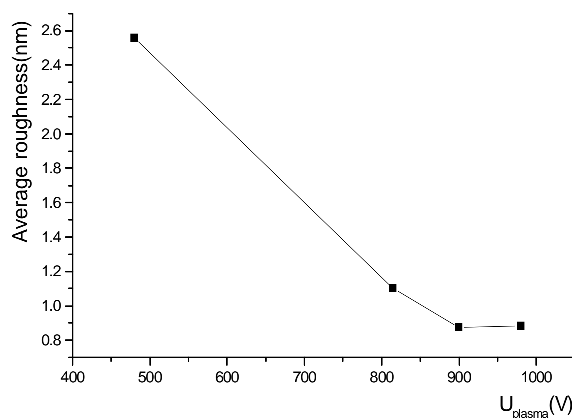

Fig. 6. Average roughness value dependence on arc voltage drop – i.e. directed energy of ions in the case of MgO layers.

3. Results and discussions

Taking into consideration the peculiarities of the carbon film deposition, we consider that TVA is one of the most adequate technologies for this field of applications. Indeed, due to the ensured high purity of the deposition process (in vacuum vessel only carbon being introduced besides refractory metals used as electrodes), completely hydrogen free carbon film can be obtained. In the same time, TVA technology ensures high value for the energy spent to heat carbon which needs temperatures higher than 4000 K. Because of vacuum conditions and high sublimation temperature of the carbon, the main energy losses are practically only by radiation. Taking into account these advantages, we used TVA for carbon evaporation and deposition.

The deposited C films were studied using TEM electronic microscopy with a magnification of 1.4 M and a resolution of 1.4 Å. The samples of deposited carbon films (deposited on NaCl or KCl monocristals, solved in water before TEM examination) show nanostructure films. The size of cylindrical structure has a diameter of 2.40-2.70 nm and a length of only 1-2 nm, that proves the nanostructure of the films, as it is shown in Fig. 7.

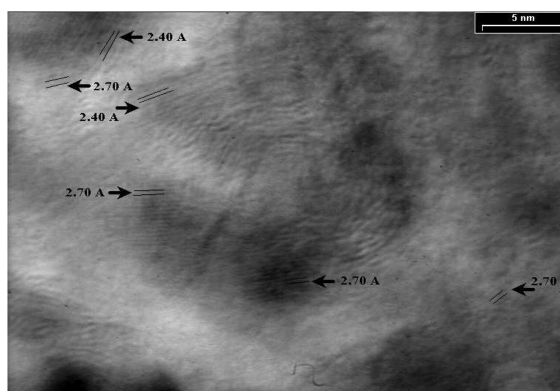

Fig. 7. Crystals surrounding by partial graphitized carbon on the amorphous carbon film.

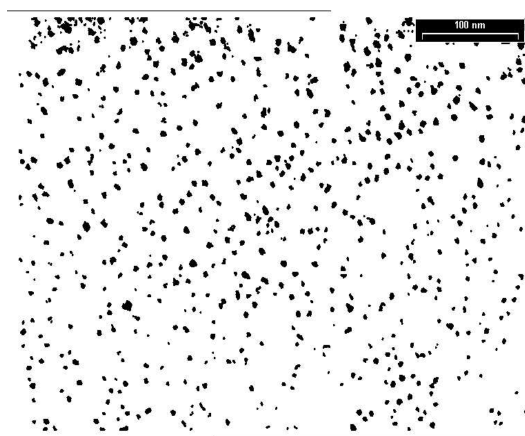

Fig. 8 a. TEM image of grains.

From the picture of grain size distribution one calculated an average value of 6.52 nm (see Fig. 8a, b). The electron diffraction pattern shows the formation of crystalline structure in the deposited thin films.

Statistical Function	Mean Diameter
Base Unit	nm
Count	492
Mean	6.52
Minimum	3.88
Maximum	15.09
Standard Deviation	1.77

Fig. 8b. Statistical functions.

The new system of deposition is peculiarly adequate for hydrogen free, high quality-smooth and compact-DLC film deposition. TVA easily ensures the needed high value of the energy to evaporate pure carbon.

4. Conclusions

Thermionic Vacuum Arc (TVA) can be used successfully for hydrogen free carbon film deposition, ensuring good qualities and high purity. Nanostructured carbon films with low value of the roughness can be obtained quite easily. Further developments will be related mainly to the improvement of the TVA stability at the transition from the heating of carbon rod by electron bombardment to the TVA plasma ignition.

References

[1] S. Ainsenberg, F. Kimock; Materials Sci. Forum, 52 & 53, Trans Tech. Switzerland, 1-40 (1990).
[2] J. Robertson, Diamond and Relat. Mater. **2**, 984 (1993).
[3] R. Vladoiu, G. Musa, I. Mustata, J. Optoelectron. Adv. Mater. **5**(1), 325 (2003).
[4] G. Musa, H. Ehrich, M. Mausbach; Journal of Vacuum Science and Technology **A12**, 2887 (1994).
[5] G. Musa, H. Ehrich, J. Schuhmann; IEEE Transactions of Plasma Science **25**, 386 (1997).
[6] H. Ehrich, J. Schuhmann, G. Musa, A. Popescu, I, Mustata; Thin Solid Films, **333**, 95 (1998).
[7] H. Ehrich, G. Musa, A. Popescu, I. Mustata, A. Salabas, M. Cretu, G. F. Leu; Thin Solid films, **332**, 1 (1998).
[8] H. Ehrich, J. Schuhmann, G. Musa, A. Popescu, I. Mustata, Thin Solid Films **333**, 95 (1998).
[9] P. Martin, IEEE Trans. Plasma Sci. PS-**18**, 885 (1990).