UNBALANCED MAGNETRON DEPOSITION OF COMPOSITE METAL/C:H FILMS–A COMPARISON OF BASIC PROPERTIES OF Ag/C:H, Ni/C:H AND Mo/C:H

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ABSTRACT: Composite metal hard/carbon films (Ag/C:H, Ni/C:H and Mo/C:H) were prepared by unbalanced magnetron sputtering using Ar and n-hexane working gas mixtures. Basic electrical and optical properties, morphology (TEM), and composition and bonding states (XPS) were studied. FTIR absorption measurements were performed to examine the C:H part of the composite. The main emphasis was on ERDA/RBS compositional depth profiles of the composite films. Maximum 15 at.% of hydrogen was found for samples that contained less than 1 at.% of the metal. The hydrogen content decreases with the increased amount of the metal and it decreases with the energy of bombarding ions. FTIR spectra show that C:H part of the composite is a mixture of amorphous carbon and polymer-like structures. Ageing process in the open air and at room temperature was studied by means of the electrical resistance and TEM observation. Phenomenological model of the ageing at ambient conditions is proposed.

I. INTRODUCTION

Metal-containing hard hydrogenated carbon (metal/C:H) films are very atractive because of their interesting optical, electrical and mechanical properties. In recent years several studies appeared (for review, see references 1,2). This research has continued using hard carbon films containig Ti,Ta,W and Te [3-5], and more lately Ag , Ni and Mo [6-8]. In many cases an unbalanced magnetron operated in a mixture of argon and a hydrocarbon gas was used for the composite film deposition (e.g. in Refs. 4, 6-8). This process is basically a co-sputtering of a metal and some carbon from the metal target, usually partially poisoned, and plasma polymerization process taking place in a gas phase (plasma volume) and on adjacent surfaces (substrate). However, the growing composite film on a substrate is subjected to an energetic positive argon and fragmented hydrocarbon ions bombardment [9]. The accelerating electric field for these ions originates from the floating potential appearing on the substrate surface when it is immersed in a plasma directed at it by the unbalanced magnetic field of the magnetron. Dielectric part of the composite converts, due to energetic ion bombardment, from a plasma polymer, with an excess of carbon, into a hard plasma polymer, for which we coin a term C:H. An additional bias can be imposed on the substrate using an auxilliary power supply. Usually rf power is used to obtain dc negative substrate bias, V_B.

The above described deposition process was used in this study for the preparation of Ag/C:H, Ni/C:H and Mo/C:H composite films. Working gas mixture of Ar and n-hexane was used. Morphology determined by TEM, basic electrical and optical properties and the ageing processes in the open atmosphere were studied, however, the main emphasis was on elastic recoil detection(ERD) analysis and Rutherford back scattering (RBS) compositional depth profiles of the composite films [10]. The bonding states of Ni and Mo, especially with carbon and oxygen, were also in the centre of the attention.

II. EXPERIMENTAL

The deposition configuration consisted of one dc unbalanced magnetron (78 mm in diameter) suspended from the top of the vacuum chamber, while the substrates rested on an rf excitation electrode of a similar size. In this case we used an Ar/n-hexane mixture. Usually, the rf power was disconnected and the isolated electrode, with substrate, was at a self bias (floating) potential developed in a plasma beam from the magnetron. In some experiments, rf power was delivered to the substrate supporting electrode for the creation of an additional dc negative self bias (up to -300 V). Typical deposition parameters were as follows:

a) For Ni/C:H and Mo/C:H the operating voltage was 400 - 450 V and 350 - 400 V respectively, The current was 200 mA in the both cases as well as following parameters : U_B= -30 V, pressure of Ar plus n-hexane was 3 mtorr, the mass flow of Ar was 1.5 SCCM, that of n-hexane is 0.55 SCCM.

b) For Ag/C:H following deposition parameters were applied : U_B= -12 V, pressure of Ar plus n-hexane was 12 mtorr, the mass flow of Ar was 2.4 SCCM, that of n-hexane was 0.4 SCCM, the operating voltage of the magnetron was between 300-440 V, with a current of 25-100 mA.

An ERDA/RBS facility [11] was used for the elemental analysis including hydrogen. The details of this method can be found elsewhere [11].The composition and atomic bonding states were studied using a VG ADES 4000 system. The film morphology was examined by means of an electron microscope TEM Jeol 2 000 FX.

Optical absorption in the visible region of light was studied using spectrometer HITACHI 3 300. FTIR absorption was observed by means of NICOLET Impact 400 spectrometer.

The changes of the film morphology and composition with the bias were observed by TEM and XPS, respectively. Ageing of the films in the open air was studied in terms of dc electrical resistance. The TEM micrographs were taken from samples deposited on carbon foils supported by copper grids.

III. RESULTS AND DISCUSSION

Morphology of the metal/ C:H samples observed in TEM reveal that the size of metal grains is between 1-10 nm. As a rule the size of metal inclusions was found decrease, at a comparable preparation conditions and metal volume fraction ratio f (filling factor), with the increasing melting point of the metal in the following sequence Ag > Ni >Mo in a agreement with [11].

Optical transmission in the visible region of light in the case of Ag/C:H deposited on glass reveals anomalous optical absorption that gives a colour appearence to the film in transmitted light [6]. This is not the case of Ni/C:H and Mo/C:H. However, the changes in transmission with time during which the sample is stored in the open atmosphere are pronounced in all three cases. These changes in optical transmission are a consequence of the morphological changes in the composite films.

In the case of Mo/C:H the electrical resistance versus filling factor reveals a substantial decrease over several orders of magnitude at the percolation threshold. Such abrupt decay starts at a filling factor of 0.3 and it extends up to 0.6. The same for Ni/C:H may be seen from 0.2 to 0.4, and it is more steep. A rather sharp percolation threshold between 0.3 and 0.4 was found for Ag/C:H.

Most effort has been devoted to ERDA/RBS depth profile analysis. As an example, Mo/C:H compositional profile is shown in Fig.1.

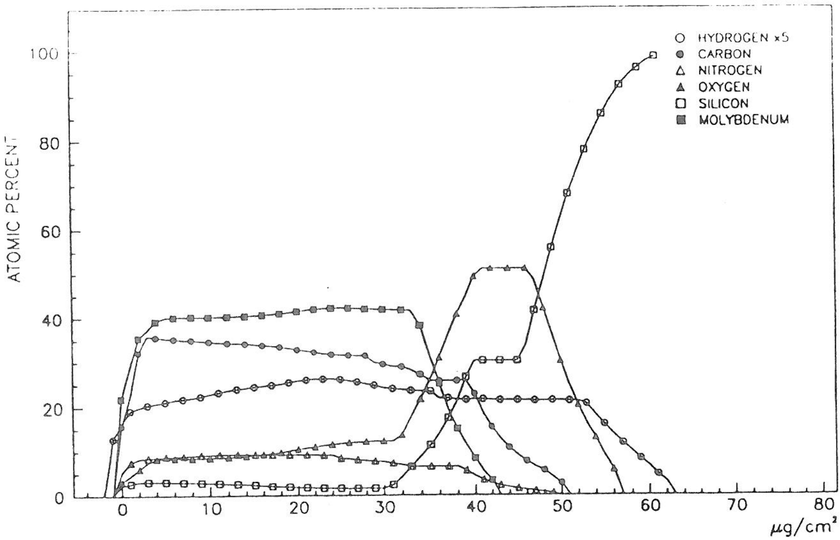

Fig.1. Concentration depth profiles by ERDA/RBS for a Mo/C:H film (thickness 100 nm).

Similar profiles were obtained for Ag /C:H and Ni/C:H. One can see that the metal and carbon concentrations are uniform through the film average. Since the films were deposited on a silicon substrate a layer of silicon oxide is always seen at the interface (between the film and the substrate). In the case of Mo/C:H the amount of hydrogen decreases with the amount of Mo and with the negative dc bias. Maximum concentration of hydrogen in the samples was 15 at. % for films containing the least amount of metal.

We also studied the C:H component of the composite. In Fig.2 the FTIR absorption spectrum of a composite with negligeble amount of Mo (deposited with totally poisoned Mo target) is shown. As far as the ageing is concerned, in most of the samples the absorption at 3450 cm^{-1} , related to OH group, and at 1700 cm^{-1} due to C=O increases pointing to an uptake of water and oxidation.

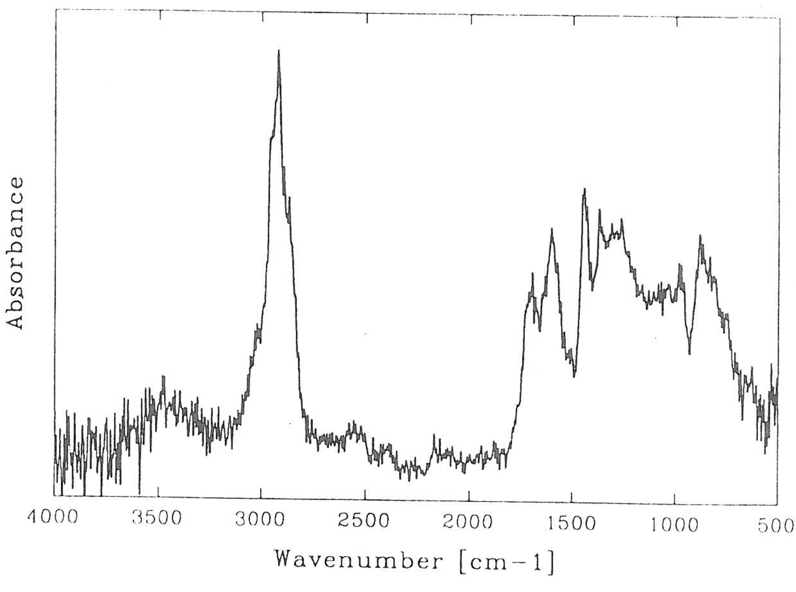

Fig. 2 Example of FTIR absorption spectrum for a Mo/C:H film (thickness 90 nm) with a negligable amount of Mo (~1at. %).

Ageing effets were confirmed by TEM and electrical resistance when the samples were stored in the open air. It has been found that the increase of resistance appears in all three types of composites . TEM micrographs, evaluated by means of optical image processing (for details, please see refs 6,7), confirmed that the size of metal grains and their distances increase in the first periode of sample storage in the open air. After several days (1~ 10 days, for Ag/C:H, and after about 30 days for Ni/C:H) a decrease of the resistance takes place [6-8]. As shown by TEM the metal grain neighbour distances decreased. This might be qualitatively explained by the rearrangement (shrinkige) of the C:H matrix. This effect does not happen for Mo/C:H where gradual and slow increase of resistance continues. In order to reveal this effect in more detail we studied an accelerated ageing by measuring the dc electrical resistance in the open air at elevated temperatures (60 and 120^0 C). Both samples are identical (they were prepared in the same run). The lower values for 120^0 C are because of negative TCR (See Fig.3).

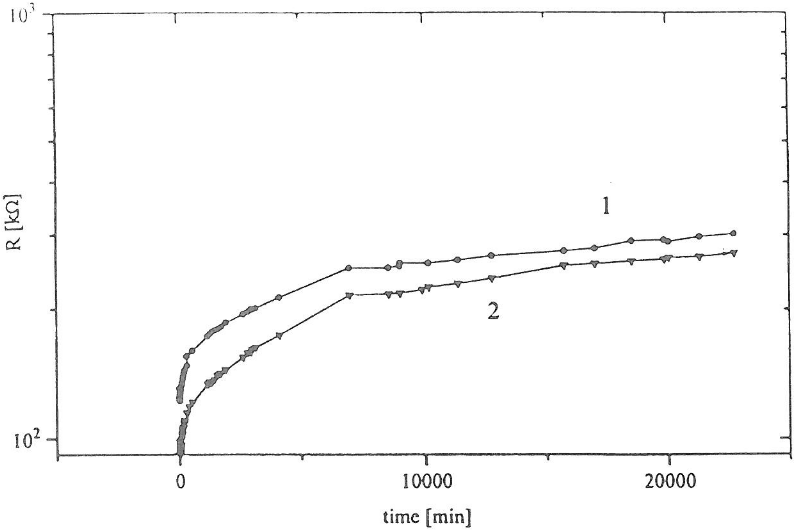

Fig 3 Resistance of Mo/C:H film (f = 0.55) kept in the open air at temperatures:333 K - curve 1 and 393 K - curve 2.

The only explanation is that in contrary to the previous two composites pronaunced oxidation processes may take place during Mo/C:H ageing. This probably prevents the C:H matrix to rearrange. This hypothesis is now under investigation using XPS analysis.

IV. CONCLUSIONS

The results of the present study may be summarised as follows:

1. The ERDA/RBS depth profiles have shown that the composite films possess uniform concentration of the metal and of other elements throughout the film thickness.

2. Hydrogen concentration decreases with the increase of negative substrate bias and/ or of the metal concentration.

3. FTIR absorption reveals that the C:H part of the composite is a mixture of amorphous carbon and polymer like structures.

4. Optical transmisson in the visible region of light for Ag/C:H reveals anomalous absorption that gives a colour to the film in transmitted light in contrary to Ni/C:H and Mo/C:H.

5. The electrical resistance decreases with increasing filling factor over several orders of magnitude for all the three composites.

6. Phenomenological model of the composite film ageing at room conditions was proposed considering diffusion of small metal particles to form larger agglomerates, and metal oxidation.

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