DEPOSITION OF COMPOSITE METAL/C:H FILMS AND THEIR BASIC PROPERTIES

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Abstract

Composite Ag/C:H films were prepared at room and decreased temperature on glass, silica and saphire substrates using an unbalanced electromagnetron with Ag target operated in Ar/n-hexane mixture. Optical transmission measurements, TEM micrographs, ac and dc electrical measurements have been used to study ageing effects of the composites.

Introduction

Studies of composite films metal/hard carbon are summarized in several reviews [1-3]. These films were likely prepared for the first time by Harding and Craig [4-6] who sputtered a post cathode from Fe, Cu in a mixture of argon/acethylene in a dc cylindrical magnetron. Several studies have appeared in subsequent years [2,3]. Laurent and Kay [7] sputtered in a simple rf diode system gold and cobalt in an argon/propane mixture. In recent years a great effort has been paid to hard carbon films containing Ti, Ta, W metals by group of Dimigen and Memming [8,9]. The first introductory studies have been also performed in case of Ag/hard carbon films [e.g. 10, 11]. The first results on graded Ti-C:H coatings and multilayers have also been published [12].

Experimental

An electromagnetron operated in an anbalanced mode was employed in a diffusion pumped stainless steel bell jar. The electromagnetron was of rectangular shape, 110 mm by 70 mm, with a soft iron magnetic circuit. Magnetic field

generation was provided by coils on the inner core and around the whole assembly. Values of current 1.6 A and 1.5 A in the inner and outer coils, respectively provided dc negative substrate bias: - 12 V . Substrate was placed in distance 50 mm below the silver target. Working gas mixture Ar/n-hexane was used. Details of the deposition apparatus may be found elswhere [11].

Results and discussion

In the first experiments we examined carbonaceous component of the composite. The films were prepared under following pressures and flow rate of gases in a working gas mixture: n-hexane (0.4 Pa and 0.4 cm^3STP/min), argon (1.35 Pa and 2.4 cm^3STP/min). Silver target was fully covered by carbon film. Discharge parameters betwen 25 mA (13,5 W) to 150 mA (79 W) were used that yielded samples with densities between 1.6 to 2 g/cm^3 and optical gaps obtained from absorption measurements of between 1.6 and 2,1 eV. Density of DLC films was found earlier between 1.5-1.8 g/cm^3 [13], optical gap for DLC films produced in an rf discharge from 2.5 eV to 1 eV [14]. However, Zou et al. [15] assigned values of densities between 1.7-2 g/cm^3 to transitional films between plasma polymer and DLC (a-C:H). We measured FTIR absorption spectra for the above described samples that show a typical DLC(a-C:H) spectrum. For samples prepared at low power a spectrum was obtained containing additional absorption at 1700 cm^{-1} assigned to double bonds in linear chains. This is a sign of increased presence of polymeric structures in these samples.

Afterwards composite films were prepared. Their FTIR absorption spectra are slightly different from those mentioned for C:H samples. However, FTIR absorption spectra do not reveal unbonded hydrogen and therefore their interpretation must be taken with a great caution [16-18]. Composite films have been prepared on silica substrates without breaking vacuum in six following runs. Working gas mixture n-hexane/argon, total pressure 2Pa and flow rates in relation 1:10 (0.24 cm^3STP/min and 2.4 cm^3STP/min) were used. Before deposition the target was cleaned by sputtering in Ar on to a shutter.

In Table 1 the samples are ordered according to magnetron power that results in 1) the enlargement of silver grains dispersed in C:H matrix and 2) increse of Ag volume fraction ratio f of the resulting composite. The latter is a consequence of steeper growth of deposition rate of Ag compared to C:H. The former may be explained as follows.

Table 1 Deposition parameters of Ag/C:H films and corresponding assessments of: volume fraction ratio f and characteristicl grain size G_s determined from TEM.

No	I(mA)	U(V)	t(nm)	f	G_s
V 3	10	292	26	>0.01	2
V 1	25	350	37	0,014	5
V 2	50	390	40	0,0245	8
V 5	100	440	42	0,08	20
V 6	200	530	40	0,24	40-50

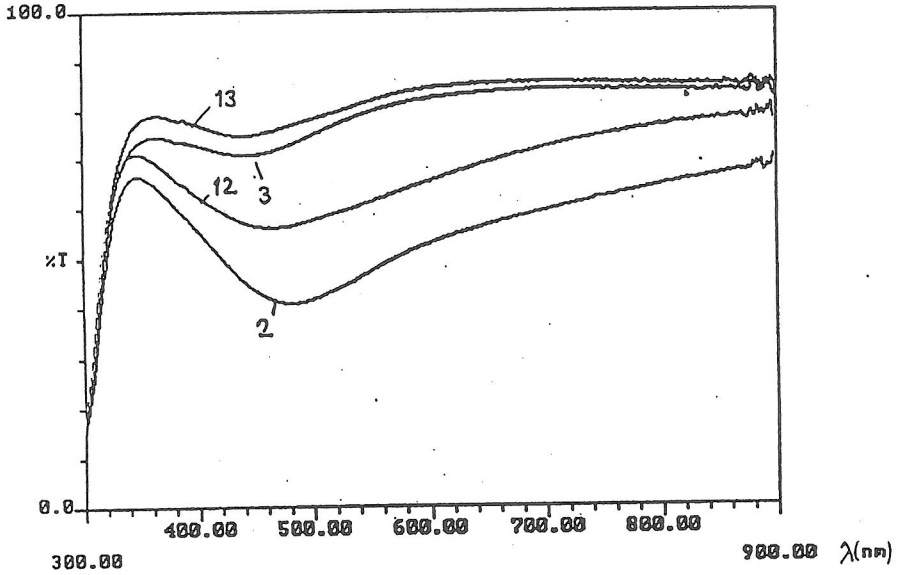

Fig.1 Transmission spectra of the samples V3 and V2 from Table 1 immediately after deposition (2, 3) and after 16 days (13, 12).

It is well known that plasma beam of an unbalanced magnetron delivers greater energy to the growing film due to ion bombardment that results in increased temperature of the film and substrate. Preliminary assessments showed that

overall substrate temperature may increase four times between samples No V3 and No V5. Kinetic energy delivered to the growing film may be also responsible for increased dimmensions of Ag grains. Both of these processes should stabilize the composite film [3,19] but we observed longer term(several days) ageing. We found using TEM that silver grains co-agulate (increase their diameter). As it has been predicted [20] this will also explain the changes in the optical transmission with time in the open air observed also in our case. (See Fig.1.) We also deposited composite films on saphire substrates at a temperature -45^{o} C. The films showed small and relatively equal size silver grains but C:H component was very different. Ageing effects observed in the optical transmission were similar to the sample V_2 but more pronaunced.

Dc electrical properties have been studied on planar and sandwich samples Ag-Ag/C:H-Ag that showed similar results. Planar samples were prepared by pre-evaporating finger-type Ag electrodes (distances: 10 mm, 5 mm, 0.05 mm) on glass substrate. Composite Ag/C:H film was deposited over these electrodes and measurements started without breaking vacuum. Samples resistance in vacuum and in the open air are given below.

Table 2 Resistance of planar samples Ag/C:H.

N_o	$R_\square$(MΩ) vacuum	$R_\square$ (MΩ) air	ESCA analysis in at.%		
			C	Ag	O
IP	0,5	2,3	63,8	16.6	19.6
IIP	27	161	75.2	5.4	19.5

V-A characteristics of these samples are sublinear and cycling the sample from vacuum to the air and back to vacuum results in overall decreased conductivity. Long term development of the resistivity of the sample in the open air shows that the original increase of resistivity that took place about a week was changed by gradual decrease.This suggests that for certain time the average distance among grains increases (smaller grains join the bigger grains and their size increases) and after a time in the open air C:H component undergoes changes that start to bring the grains in average closer again.

We have done also ac measurements using HP4192 ALF impedance analyser and LCR Meters HP 42 74 A and 42 75 A. For this purpose we have prepared sandwich samples in the following way. On preevaporated Ag electrode we deposited composite film Ag/C:H. Without breaking vacuum we cleaned silver target by sputtering it into shutter using pure Ar and then sputtered top Ag electrodes and started ac measurements of real and imaginary parts of permitivity. The two relaxation maxima seem to appear in the immaginary part of permitivity between 10^2Hz and 10^5Hz. The first maximum develops with time in the open air and may be associated with water wapour. The example of the ac measurements after storing the sample in the open air for 9 days is in Fig. 3. This confirms polymeric nature of C:H component of the composite.

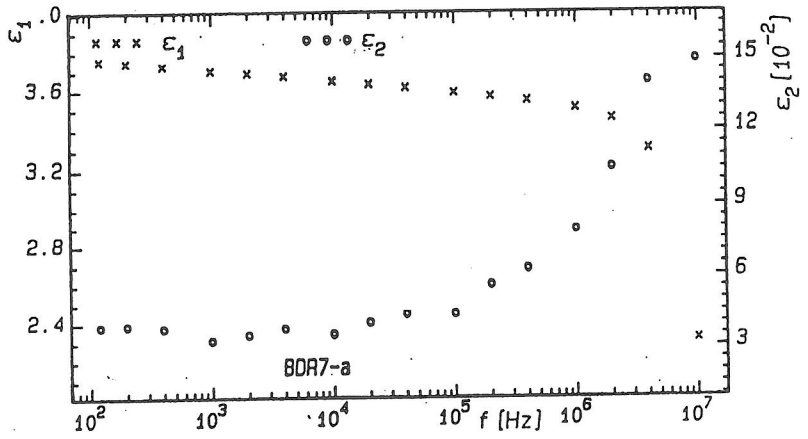

Fig.2. Ac electrical measurement of Ag/C:H sample prepared at discharge current (power): 100 mA (36 W).

Several composite films Ag/a-C:H were deposited with dc negative self bias imposed to isolated substrate holder from auxiliary rf power supply. These films posses high hardness, however, high stress. Experiments started also with Ni/C:H composite films and the investigation is in progress.

Conclusions

It has been shown that the dielectric part of the composite silver/hard carbon prepared by unbalanced electromagnetron only is a hard polymer(C:H). Ageing observed in the optical transmission and TEM can be explained in terms of silver

grain growth with time. The dc electrical measurements are in accord with this idea for the starting period of ageing. First ac measurements also pointed out on polymeric character of C:H.

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