

Unstressed carbon-metal films deposited by thermionic vacuum arc method

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A novel method based on thermo-ionic vacuum arc plasma was developed to grow metal-carbon zero stress films for MEMS applications. The method chosen to prepare metal-carbon films uses an electron beam emitted by an externally heated cathode accelerated by a high anodic voltage. Applying a high voltage (1-6 kV) between cathode and anode bright plasma was ignited in carbon atoms. In order to minimize the internal stress and to get films with increased adherence, interlayer and graded interlayer with Fe, Cr, Al and Ni was deposited. The prepared films were characterized by XPS, XRD, AFM and ellipsometry.

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1. Introduction

The continuous development of technology is based on new materials with improved properties used in highly performing devices. One of the most interesting materials nowadays is metal-carbon (carbon) film used for Micro-Electro-Mechanical-Systems (MEMS) applications. MEMS is about 80% based on Si. Even Si can be used in many applications, its usage is limited due to the low mechanical and high wear resistances and high coefficient of friction between Si and SiO₂. These problems can be solved by using new materials with enhanced tribological properties [1-2] ensuring lubrication and hydrofobicity to prevent adhesion. Research on developing new carbon films production technologies is still undergoing, as adhesion failure (due to the residual stress during deposition), the impossibility of uniform deposition of carbon film on large areas and the high production costs are the most important factors limiting the performance of these films.

An important amount of work is presently dedicated at studying synthesis of high quality carbon films using different methods like: magnetron sputtering, chemical and plasma vapor deposition (CVD and PACVD, respectively), electron cyclotron resonance (ECR), filtered cathodic vacuum arc (FCVA), ion beam sputtering, pulsed laser deposition (PLD), ion Beam sputtering etc.

The present work is aimed at promoting a novel technique called thermo-ionic vacuum arc (TVA) [3-9] for deposition of zero stress, smooth, thin, continuous, high sp³ content metal-carbon (carbon) nanostructured-coatings compatible with silicon processing technologies.

The method chosen to prepare carbon films uses an electron beam emitted by an externally heated cathode (a grounded tungsten filament) accelerated by a high anodic

voltage. The electron beams provided by a TVA gun evaporates the graphite anode. Applying a high voltage (1-6 kV) between cathode and anode was ignited bright plasma in pure carbon atoms. The plasma was controlled by the electron beam emitted by the heated cathode (thermo-electrons). Taking into account that the TVA method do not implies hydrogen containing precursors (as for example the CVD method that uses hydrocarbons as e.g. CH₄) one expects to obtain carbon films with a minimal stress. In order to minimize the internal stress and to obtain films with increased adherence, interlayer and graded interlayer as Fe, Cr, Al and Ni was deposited by simultaneously evaporation of these metals using another TVA gun. The process parameters were studied and optimized.

2. Experimental set-up

One of the most important characteristics of TVA method is the presence of energetic ions in the pure carbon and metal vapor plasmas, respectively. Moreover, the energy of ions can be fully controlled from outside of the discharge vessel via the control of the arc voltage drop value. It results that during film preparation, just during deposition, the growing thin film is bombarded by energetic ions with an in advance established value of the energy of ions. The bombarding ions are just the ions of the depositing material (carbon and metal). A Wienelt cylinder is used to focus the electrons on the anode surface. The experimental set-up is shown in Fig. 1. A bright discharge is established in high vacuum conditions in the cathode-anode space. Due to the high energy dissipated in the unit volume plasma, the material is strongly dispersed and completely droplets free. The obtained thin film was

very smooth and in some experimental conditions had a nano-scale structure.

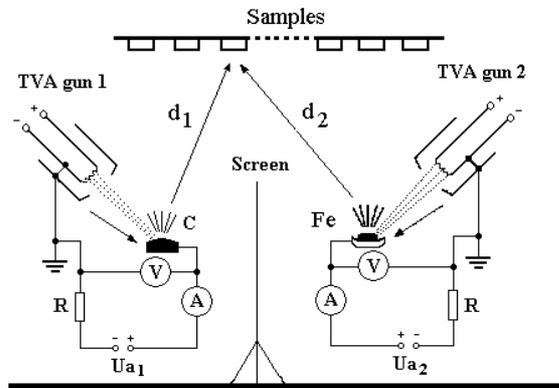


Fig. 1. Experimental set-up for metal-carbon deposition.

Coatings on mirror-polished Si (size of 10 mm × 10 mm × 0.5 mm) and glass substrates (size of 8 mm × 60 mm × 0.5 mm) were performed. The main working parameters are presented below. Anode material is a graphite rod of 10 mm diameter and 200 mm in length and 99.99% purity metal flakes of Fe, Cr, Al and Ni. Cathode material is W + 0.2% Th of 1.5 mm in diameter. The distance between cathode and anode is 2–10 mm. The angle between the electron beam and the horizontal line is 30–45°. The intensity of the heating current of the cathode filament is 100–120 A. TVA applied voltage is 1–6 kV; TVA discharge voltage is 1.5–2 kV. The intensity of the TVA current is 0.1–1 A. The distance between anode and substrate holder is 100–300 mm. The deposition rate is 0.2–3 nm/s.

The residual stress was evaluated by studying the X-ray diffraction spectrum (XRD) of Si substrate before and after deposition. The films were characterized by transmission electron and atomic force microscopies (TEM and AFM) and the refractive index was evaluated by ellipsometry. The chemical resistance was tested using corrosion resistance against the chemical agents used in microelectronic processing technologies.

3. Results and discussion

XPS investigations of the C1s peak lead to a sp^3 carbon bond content of approximately 89% for a pure carbon coating. This value was evaluated by fitting the C1s peak with the two main components, diamond represented by sp^3 bonding (peak at 285.4 eV) and graphite represented by sp^2 bonding (peak at 284.4 eV), and by calculating the area under the peaks [10]. Furthermore, a small content of C–O bonding at 288.5 eV was detected. The XPS spectrum of the film and the deconvolution in sp^3 and sp^2 correspondent contents are shown in Fig. 2. The relatively high sp^3 contents of the coating are in agreement with Tay's observation [11], who obtained about 80% of the sp^3 bonding using Filtered Cathodic Vacuum Arc (FCVA) technique.

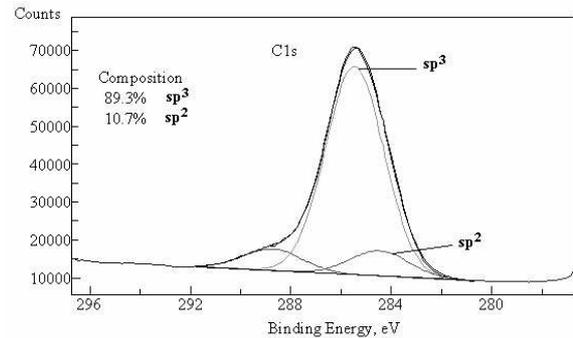


Fig. 2. C1s peak deconvolution.

High resolution transmission electron microscopy (HRTEM) images analysis shows the interference fringes given by the complex crystallites included into the amorphous carbon (Fig. 3). The arrows show the interplanar distances corresponding to the crystalline structure. The particles, 3–11 nm in diameter, were embedded into the film containing amorphous carbon. Rhomboedral structure with lattice parameters: $a = 0.25221$ nm, $c = 4.3245$ nm (ASTM pattern: 79-1473) of diamond/carbon has been obtained from selected electron diffraction pattern (SAED), as it is shown in Fig. 4.

The atomic force microscopy (AFM) image presented in Fig. 5 shows the carbon film surface with a peak-to-valley roughness within 2–3 nm range.

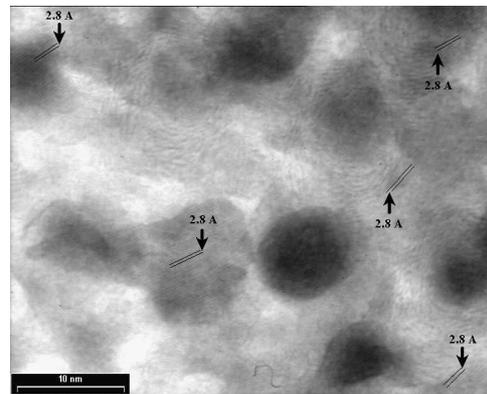


Fig. 3. HRTEM image of the carbon film. The arrows indicate the interplanar distance corresponding to the crystalline structures.

An important characteristic appearing in carbon coatings is those of the film adhesion. The adhesion of the film to the substrate is very close related on the stress magnitude and the micro-structural defects at the interface film-substrate, appearing particularly at high temperature depositions. A general conclusion on the stress level of the coatings prepared by different methods shows that by chemical vapor deposition (CVD) techniques the stress levels are larger compared with that of the coatings prepared by physical vapor depositions (PVD). This is because the substrate is heated when are using CVD methods.

Thermal stress appears just after the deposition, during cooling, when the thermal expansion coefficient is very much different from those of the substrate. The stress can be of tensile or compression type. The former can be generated by small holes, pores in substrate and the latter, found particularly to the PVD coatings, can be produced by the high energy of the particles bombarding the film during deposition. Lowering of the compression stress can be achieved by using deposition methods where the working pressure is as low as possible. The TVA method has a high potential to obtain films with low (or zero stress) because do not use any buffer gas and the processing pressure is at the order of 10^{-4} Pa.

Internal stress is an important parameter due to the fact that the maximum admissible thickness depends on it. This is important for avoiding the peeling of the deposited layer. Measurement of the residual stress can be made using X-ray techniques in the frame of the $\sin^2\psi$ method based on the study of the crystallographic planes [12]. Another technique is based on the study of the full width at high maximum (FWHM) of the XRD peaks [13].

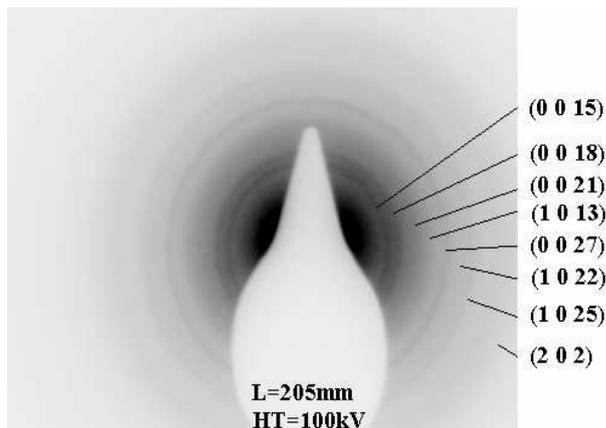


Fig. 4. Rhombohedra structures of the film with following parameters: $a = 0.25221$ nm, $c = 4.3245$ nm (ASTM pattern: 79 - 1473) corresponding to diamond / carbon, determined by SAED.

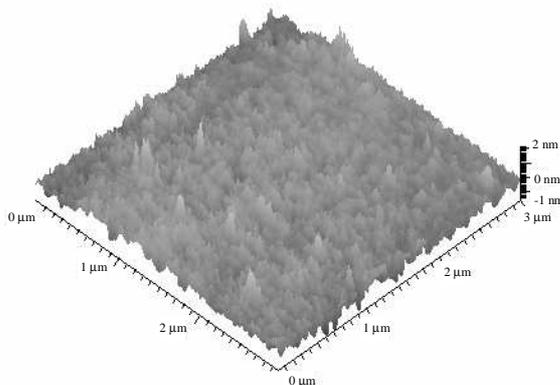


Fig. 5. AFM image of the analyzed carbon film.

In order to obtain zero stress coatings were prepared films deposited on silicon, glass and stainless steel. The process parameters were arranged in the following range: inter-electrode distance: 2-10 mm; TVA discharge current: 0.8 – 2 A, TVA discharge potential: 800 – 2000 V; filament heating current: 80 – 120 A, working pressure $< 5 \times 10^{-4}$ Pa, deposition time: 120 – 250 s.

For stress release, the carbon films were doped with metals by simultaneous deposition of Fe, Cr, Al, or Cr/Al.

As an example, the Fe-C films deposited on Si wafers were analyzed by XRD using a diffractometer TUR-M62 type with Cu anticathode.

The XRD pattern revealed the peaks corresponding to the Si substrate, the peaks induced by Fe were not observed.

The stress induced by the Fe-C coating on the Si substrate were analyzed on the basis of the special measurements when the Bragg angle is maintained constant on the position of the peak corresponding to Si (100) and the sample is rotated around the central axis of the diffractometer. In this way was determined from the profile of the Si (100) peak the degree of deformation of the Si wafer.

The measurement was made in the range of $-0.11^\circ \rightarrow +0.89^\circ$ for the uncoated and Fe-C coated Si wafer.

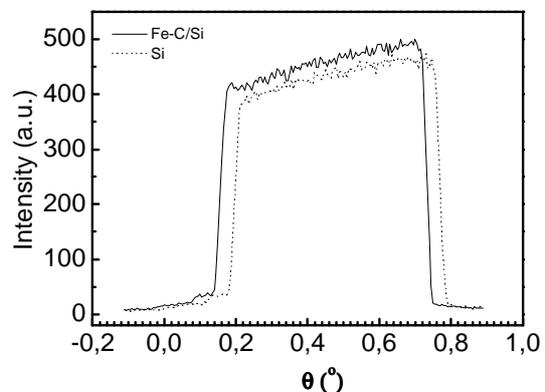


Fig. 6. The profile of the X-ray diffraction on the atomic plane Si (100) when the detector was maintained on the position corresponding to the Bragg reflexion and the sample was rotated around this position.

From the results shown in Fig. 6 we can see that after Fe-C deposition on Si the position of the peak Si (100) is shifted with 0.041 degrees compared with those of the uncoated Si wafer. Also, can be observed that the FWHM of the Si (100) peak does not change (under the limit of the experimental errors). The very low shift and practically no change in the FWHM of the Si (100) peak allow to conclude that the Fe-C coating do not produce significant stress in the Si wafer.

In order to determine the possibility to use the prepared coatings for MEMS applications the films were immersed in the most common chemical agents used in the silicon technologies. The result of the tests, presented in Table 1 shows that the Fe-C coatings are more appropriate for use with these technologies.

Table 1. The results after immersion of the prepared samples in some chemical agents.

Sample	Acetone	Alcohol isopropyl	NH ₃ 25%	NaOH 50%	KOH 50%
Fe-C	No corrosion	No corrosion	Slight corrosion	Moderate Corrosion	Moderate corrosion
Ni-C	No corrosion	No corrosion	Slight corrosion	Significant corrosion	Significant corrosion
Al-C	No corrosion	No corrosion	Slight corrosion	Significant corrosion	Significant corrosion
Cr-Al-C	Significant Corrosion	No corrosion	Slight corrosion	Significant Corrosion	Significant corrosion

Using an ellipsometer EL X-01R type, a laser wavelength of 632.8 nm and an incidence angle of 70 degree, the refraction indices were found in the range of 1.2 – 1.48.

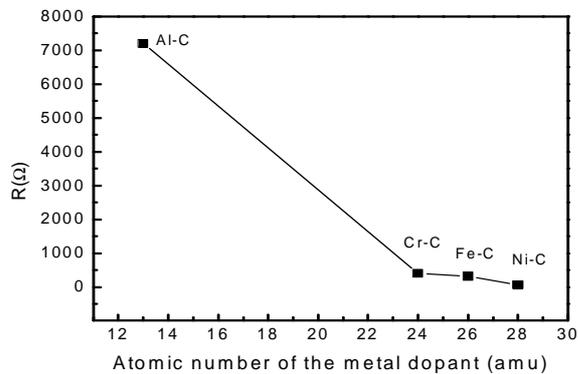


Fig. 7. Resistance of the metal-carbon coatings. The distance between the conductive samples is 5 mm.

The ohmic resistance of the coatings on the Si wafers was measured between 2 conductive probes situated at 5 mm from the each to other. The resistance of the prepared coatings was found to decrease almost linearly with the atomic number of the additive atoms in the carbon film. (Fig. 7).

4. Conclusions

One concludes that TVA method can be used successfully for preparation of zero stress metal-carbon films for MEMS applications. High resolution TEM images of the prepared films using TVA method reveal nano-structured particles with 3-11 nm diameter size,

embedded in the amorphous carbon film. The obtained films are smooth with an average roughness of 2-3 nm. The zero stress films revealed by a XRD method were obtained using metal (Fe, Cr, Ni, Al) as dopants. The Fe-C films exhibited higher resistance to some chemical agents used in microelectronics technologies and the electric resistance was found to decrease with the atomic number of the metal additive.

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