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Improved adhesion of DLC films on copper substrates by preimplantation

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ABSTRACT

The adhesion of diamond-like carbon (DLC) films on copper substrates is usually very poor. However, the adhesive strength of the films can be improved by a preimplantation step. With plasma based ion implantation and deposition, the preimplantation step and the film deposition can be realized with the same experimental setup. The effect of the implantation of several different gaseous species (N_2, O_2, Ar, CO_2, C_2H_4, and air) at −10 kV was investigated. For O_2, N_2 and C_2H_4 the influence of the pulse voltage (−5, −10, −15 kV) was examined. The samples were characterized by elemental depth profiling (XPS, SIMS), and the adhesion was evaluated with a pull tester.

Most of the preimplantation treatments increase the adhesion of the DLC films on the copper substrates considerably to values of 10–15 MPa. The best result was obtained with −15 kV oxygen preimplantation.

1. Introduction

Copper is one of the materials which are used for the production of microelectromechanical systems (MEMS) [1]. In cases where a lower friction coefficient or a higher hardness of the surface is required, a surface coating of diamond-like carbon (DLC) is advantageous [2,3]. Since MEMS consist of small complex shaped features, e.g. micro-trenches, a coating technique that is applicable for three dimensional coatings is mandatory. Plasma based ion implantation and deposition (PBII&D) is a well suited preparation technique under those circumstances. Furthermore, it also opens the possibilities to coat larger interior structures for other applications, e.g. the inner wall of tubing [4]. A DLC coating on the inside of copper tubes provides an enhanced resistance to wear and corrosion. However, the adhesion of DLC films on a copper surface is poor, and delamination of the DLC film is a frequent problem [2]. Hence, a pretreatment of the copper substrate is necessary to increase the adhesion of the DLC film. One possibility is the deposition of interlayers, e.g. Si [5], SiC [6], Ti, TiC, TiN and combinations thereof [7,8], sometimes with additional intermediate layers [9]. This requires additional hardware, though, like sputter sources or plasma arc sources. Depending on the setup, the three dimensional coating capability might be lost. Another possibility to increase the adhesion is surface nanocrystallization which relies on the effect of a mechanical surface treatment [10]. As such its unsuitability for complex shaped samples is obvious. So, a pretreatment step by PBII would be a simple solution to increase the adhesion. A preimplantation step is likely to reduce the number of contaminants on the surface and change the surface roughness because of the sputtering taking place. While some roughness is favorable for the adhesion, a too intense roughening will weaken the adhesion [11,12]. Additionally, the chemical bonding in the interface layer can be changed by implanting atoms into the surface. A carbon gradient layer, which can be obtained by the implantation of a hydrocarbon, shows good results on a number of substrates [13,14] but not on copper [13]. Tonosaki et al. [2] reported that a preimplantation with oxygen allowed the deposition of DLC films on copper, without providing the full experimental details. They used an RF generated plasma with high voltage pulses of −20 kV (although the corresponding figure shows only −18 kV) for 20 µs with a repetition rate of 1 kHz, without providing a value for the pressure. CH_4 was used for the deposition process.

An earlier paper on the commercial applications of ion beam deposited DLC coatings reported excellent adhesion of the coating on copper (with contradicting values reported for the pull test with 1.6 N/m^2 (~1.6 × 10^{-6} MPa) and 8000 psi (~55 MPa), though) [15]. However, it is not clear from the experimental description whether the DLC coating was deposited directly onto the copper; since the coatings were described as similar, but not identical, to those of Marotta et al. [16] – who used Ni and a-Si:H interlayers – it is likely that interlayers were also involved in [15].

One property of copper that might lead to a complication is its sputtering yield. Not only is the sputtering yield relatively high [17] but also it depends heavily on the crystallographic orientation [18]. Using polycrystalline copper, the amount of implanted material changes with grain orientation; in cases where the crystallite size is in the mm range or above and the color of the substrate is altered by the implantation, e.g. with oxygen [2] or carbon [19], this is visible to the naked eye. Performing electron backscatter diffraction (EBSD) measurements, a link between grain orientation, sputter rate, and amount of implanted species can be found [20]. Since the adhesive strength of the DLC layer

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depends on the distribution of the implanted species inside of the substrate, the latter will change with crystallographic orientation, even if identical experimental parameters are used for the implantation process.

So, a copper substrate is not easily treated and there are only few and partial data to be found. This being the case, the implantation of oxygen and other gaseous species was tested under different experimental conditions. Then the adhesion was evaluated with a pull test. Usually methane (CH_4) is used for implantation [21], while the preparation of DLC films via PBII is done with acetylene (C_2H_2), toluene (C_7H_8) or benzene (C_6H_6) [22]. Here, ethylene (C_2H_4) was used for the deposition and also for some of the implantation experiments.

2. Experimental

Polycrystalline copper with 99.95% purity was used as substrate. It was cut into pieces with sizes of 10 × 10 × 0.5 and 15 × 15 × 0.5 mm, polished to a mirror finish and ultrasonically cleaned in ethanol for 15 min at room temperature. After drying under a stream of heated air the samples were fixed to a metallic holder with 10 cm diameter via small screws. Additionally, pieces of silicon (about 20 × 20 mm) that were cut from a wafer were also fixed to the holder and treated simultaneously. The silicon pieces provided comparison samples that facilitate analysis, e.g. to check the homogeneity of the DLC film with depth.

The implantation and deposition was done in a high vacuum chamber with a base pressure of 10^{-4} Pa or better. The plasma was generated by a high voltage pulse applied to the sample holder, i.e. there was no additional plasma source. As a consequence, the number of ions generated will not only depend on experimental conditions like gas pressure and quantity of the high voltage but also on the type of gas itself. Important factors influencing the number of generated ions are the collision-cross section and the ionization energy of the atoms or molecules [23]. In cases of mixtures of gases additional processes like penning ionization might happen. Several separate gas feeds equipped with mass flow controllers were used to feed the gases into the chamber. The gases used were N_2, O_2, Ar, CO_2 and C_2H_4, with a purity of 99.9% or better, and normal lab air. The flow rate was 10 sccm; in the case of the combination of two gases each gas possessed a flow rate of 5 sccm. A schematic of the experimental setup can be found in [24]. The implantation was performed at a pressure of 0.7 Pa with high voltage pulses of −5, −10 and −15 kV. The pulse length was 10 μs, and the repetition rate 2000 Hz, with a treatment time of 15, 30 or 45 min. Shorter times were utilized in the case of a higher sputter yield (Ar, 30 min) and in the case of C_2H_4 (15 min) since here the implantation treatment passes over into film deposition.

The DLC films were deposited in a C_2H_4 atmosphere at 0.7 Pa (flow rate of 6 sccm), with high voltage pulse of −15 kV with 40 μs length and a repetition rate of 250 Hz for 45 min. The deposition results in DLC films with the following properties (provided that a flat substrate such as Si is used): a surface roughness of $R_a = 0.43$ nm as obtained from AFM measurements; an intensity ratio I(D)/I(G) from Raman measurements of 2.6; a hardness of 17.7 GPa as obtained by nanoindentation; and a friction coefficient of 0.09 from a ball-on-disk test (6 mm diameter WC ball with a load of 1 N, 100 mm/s at room temperature at 25% humidity). On the copper substrates some properties of the DLC film, e.g. the surface roughness, will be different because of the initial roughness of the substrate and the subsequent roughening by sputtering.

The substrate temperature after implantation and deposition is not easily measured [25] because of the applied high voltage. Similar experiments with the same experimental setup which included thermal tape for temperature indication suggest a temperature below 100 °C after implantation and below 150 °C after deposition.

The film and interface region was depth profiled by XPS (2 keV Ar ions) and SIMS (5 keV Cs primary ions, positive secondary ions). The adhesive strength was measured with a pull tester (Quad Group Sebastian V). A small Al stud was glued to the surface with an epoxy resin and afterwards the pull force (perpendicular to the substrate) was registered at which the layer delaminated.

3. Results and discussion

The DLC films were all prepared under the same conditions. They were 150 nm thick and homogeneous in composition with depth, see Fig. 1 for SIMS depth profiles of samples with Si and Cu substrates. The intensities shown are from the atomic ions X^+; cluster signals of the type CsX^+ were also recorded. Since they proved to be similar, they are not shown here. The signals from the hydrogen and carbon are nearly constant and parallel to each other within the film. In the interface they decrease, whereas the substrate intensity increases. There is a difference between the two profiles in that the interface is much sharper in the case of the silicon substrate. More importantly, the oxygen implantation peak can easily be seen in the silicon surface, whereas it is nearly unrecognizable in the copper. Two reasons might cause this difference: on the one hand the silicon substrate is much smoother than a polished copper surface, thus the resolution in depth profiling will be higher for the smoother substrate; on the other hand the sputtering rate of the copper is larger than that of the silicon. In simulations with the software SRIM (Stopping and Range of Ions in Matter, version 2008.03) the sputtering yield of Cu under 5 keV oxygen bombardment is 3.6, while it is only 0.5 for Si. For the oxides (Cu_2O, SiO_2) the sputtering yield is still 2.5 times larger for the copper. Hence, more of the implanted

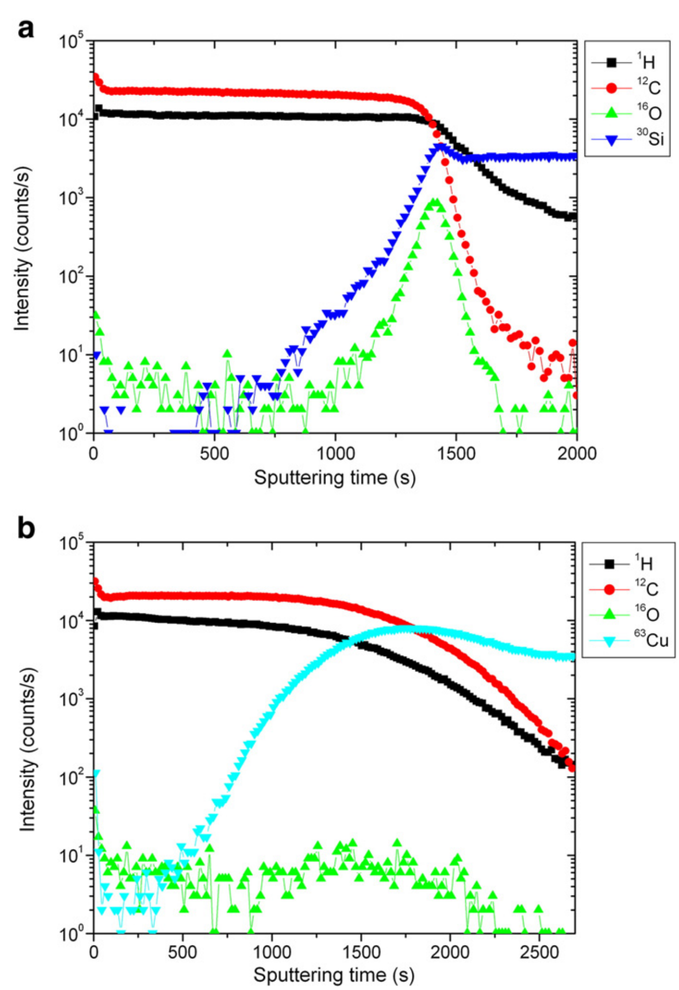

Fig. 1. SIMS depth profile of a sample with O_2 preimplantation (10 kV for 45 min with 10 μs pulse length and 2000 Hz pulse repetition rate). (a) Silicon substrate and (b) copper substrate.