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Nickel containing diamond like carbon thin films

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ABSTRACT

Diamond like carbon (DLC) coatings are well established for multiple applications. The electrical conductivity of DLC or amorphous carbon can be influenced by several orders of magnitude via doping with different metals. Depending on the deposition process hydrogen may be incorporated as well, thereby decreasing the conductivity. Recent investigations of DLC disclose nice piezoresistive properties. Our work was focused on Ni:a-C:H thin films on different substrates by reactive sputtering from a nickel target. Several carbon precursors were added to the sputtering gas to create an amorphous carbon hydrogen network with embedded crystal clusters. In order to optimize the piezoresistive properties we varied various process parameters. The piezoresistive response was monitored by measuring the resistance change during bending. Our Ni:a-C:H films develop gauge factors of approx. 12 in a wide range of process parameters.

For sensor applications the temperature coefficient of resistance (TCR) is important as well. It depends on the metal concentration in the thin film and can be adjusted by the concentration of the incorporated nickel. It can be set to approximately zero in a wide temperature range of 80–400 K. The combination of a high gauge factor and a very small TCR is achieved and described in this paper.

XRD measurements reveal nickel or nickel carbide clusters with diameters of approx. 8–30 nm depending on the metal concentration. The clusters crystallize in the hexagonal hcp structure which could be transformed into the cubic fcc structure of nickel by thermal annealing in a vacuum.

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1. Introduction

Thin films of amorphous carbon have attracted the attention of researches for decades. If the carbon has a significant fraction of sp^3 bonds it is most often termed as diamond like carbon (DLC) which can have high mechanical hardness, chemical inertness and optical transparency attributed to a wide band gap. DLC films have widespread applications as protective coatings such as magnetic storage discs, optical windows, car parts and biomedical implants [1]. The electrical conductivity of amorphous carbon films may be influenced by up to 12 orders of magnitude – from an insulator to a metallic conductor – by adding metal atoms into the growing films as demonstrated by Köberle [2] for the elements Au and Ta. The metal atoms are not homogeneously distributed in the carbon or hydrogenated carbon material, instead metal clusters or metal carbide clusters are formed due to the aggregation processes during the formation of the film. The clusters having diameters of about some nanometers and separations which are dependent on the metal concentration are revealed by transmission electron microscopy (TEM) and X-ray diffraction (XRD) [3,4]. This heterogeneous material consists of crystalline conducting clusters embedded in a more or less insulating matrix of amorphous carbon which may be hydrogenated as well (Me:a-C:H). Tunneling or hopping of the carriers between the metallic islands was suggested as the dominant conduction process. The piezoresistive effect of a-C and a-C:H films was discovered by Luetje [5,6] showing a relative high change of resistivity due to the pressure upon the films. Gauge factors of 60 and even 1000 were demonstrated recently [7] for a-C and a-C:H revealing the high potential for force and pressure sensor applications. These semi-conducting films, on the other hand, have a very high temperature dependent resistivity (negative TCR) as well, which would be a critical drawback for applications as a sensor material. Our results show, how to combine an enhanced gauge factor with a temperature coefficient of resistance (TCR) of nearly zero, making the material very desirable for sensor applications.

2. Experimental

We use a combined process (Fig. 1) consisting of the sputtering of a metallic target (nickel) and a PECVD process. A carbon containing gas, such as C_2H_2, C_2H_4 or C_2H_6, is mixed with a low

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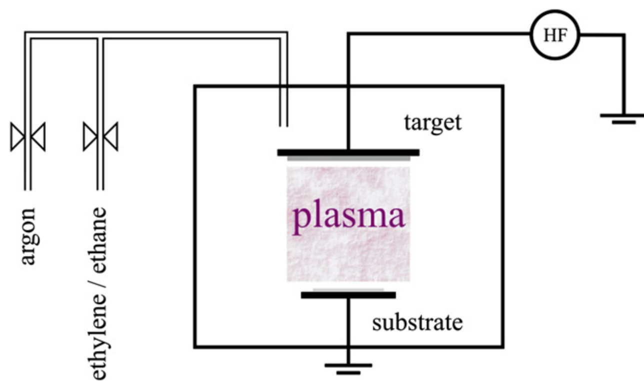

Fig. 1. Schematic illustration of the experimental setup used for reactive sputtering.

percentage into the argon gas used for sputtering a metallic target. Basically the deposition is made up of two different processes if a radio frequency power source is driving the target. The metal is sputtered by the ionized argon delivering metal atoms to the substrate. Simultaneously the precursor gas is decomposed by the plasma, building up a thin film of hydrogenated amorphous carbon on the substrate. Due to the energy intake by the particles (neutrals and ions) the mobility of the metal atoms on the carbon surface is high, leading to a cluster formation of the metal within the network of amorphous carbon. As a result, clusters of a mean diameter are embedded within the matrix. The amorphous matrix on the other hand is more or less insulating depending on the fraction of sp^3 and sp^2 bonded carbon.

It seems obvious, that a lot of parameters may influence both the matrix evolution and the cluster formation.

Prior to the deposition, the vacuum chamber was evacuated to a background pressure below 8×10^{-5} Pa in order to prevent contamination of the films. The substrates (Al_2O_3 ceramics, $20\times60\times0.4$ mm^3 for measuring the gauge factor and TCR; Si substrates, $10\times10\times0.5$ mm^3 for SEM, EDX and XRD measurements) were preheated in a load lock to approx. 100 °C before sputtering in the vacuum chamber. The total pressure was set to 3.2 Pa during sputtering with a gas mixture of Argon (99.999% purity) and carbon containing reactive gas (C_2H_4 or C_2H_6; 99.95% purity). The flow of the sputtering gas was controlled by a mass flow controller, while the varying amount of reactive gas was added by a needle valve. Monitoring the percentage of the reactive gas was performed with a differentially pumped quadrupole mass spectrometer (Pfeiffer Prisma). The reactive gas flux was varied in order to discover dependencies of the TCR and the gauge factor. The reactive gas flux was varied in a range from 0 to 2 sccm (i.e. flux ratio 0–6% of 34 sccm argon), while the other parameters were fixed. The total pressure in the vacuum chamber was fixed to 3.2 Pa for all depositions and the sputtering time was kept constant (30 min). The resultant film thicknesses range from 750 to 950 nm, because the deposition rate varies with the reactive gas (ethylene or ethane) concentration [8]. The substrate bias voltage was fixed to 100 V and the target self-bias voltage was set to −1700 V. The sputtering power increases thereby from approx. 380 W to 500 W with increasing ethylene (or ethane) concentration.

Wet etching of Ni:a-C:H thin films is not possible, hence we patterned the resistors during the sputtering process using a shadow mask. The resultant resistors have typical dimensions of 10×10 mm^2 and we arranged three of them on one substrate. For the electrical connection, the conductive paths and pads were sputtered and patterned onto the Al_2O_3 substrates before sputtering the Ni:a-C:H thin films. The pads and paths consist of a patterned CrNi/FeNi/Au layer system. The electrical connections were performed by soldering wire leads onto the pads.

After deposition the thin films were annealed at 180 °C for 3 h in the air in order to stabilise the resistors. Before and after this heat treatment, resistance measurements were carried out. The gauge factor and temperature coefficient of resistance (TCR) were measured subsequently. By bending the samples to an accurately defined radius r of 750 mm, the gauge factor (k) can be calculated from the resistance change ΔR with $k=[\Delta R\cdot 2\cdot r]/[R\cdot d]$ where d represents the thickness of the substrate and R the resistance of the thin film [8]. The temperature coefficient of resistance was measured by monitoring the resistance at different temperatures without any load. These measurements were performed in a temperature range of 90–400 K. The TCR was calculated using $\mathrm{TCR}=[R(T)-R(35\,°\mathrm{C})]/[R(35\,°\mathrm{C})\cdot\Delta T]$ at different temperatures T.

Energy dispersive X-ray analysis (EDX) measurements for specifying the metal content in the thin films were performed by using an Oxford Inka 300 spectrometer on a scanning electron microscope (SEM) of the type JEOL 6460LV. This scanning electron microscope is also used for measuring the film thickness. A Bruker D8-Focus X-ray diffraction measurement system (using Cu radiation) was used to analyse the crystal structure.

3. Results and discussion

3.1. Temperature coefficient and gauge factor

In order to investigate the dependencies of the gauge factor and the TCR from the sputtering parameters, the metal content of two series of Ni:a-C:H films, measured by means of EDX, versus the ethylene (or ethane) concentration is presented in Fig. 2.

With increasing ethylene (or ethane) concentration, the nickel content in the thin films decreases. The temperature coefficient is directly dependent on the metal concentration. It varies from positive values at high metal concentrations to negative values at metal concentrations below (50 ± 2.5) at.% as indicated by the values on the curves of Fig. 2. Independent of the species of the reactive gas (ethylene or ethane) and other parameters, the TCR can be set to zero at approx. 50 at.% nickel in the film. Using a target self-bias voltage of −1700 V, an ethane concentration of 3% yields a TCR = (0 ± 50) ppm/K, however only 2.5% are needed if using ethylene.

The reactive gas flux ratio or rather the metal content controls the film conductivity as depicted in Fig. 3. The values cover a range of six orders of magnitude from 10^3 (Ω cm)$^{-1}$ to 10^{-3} (Ω cm)$^{-1}$. At approx. 75 at.% of metal concentration percolation appears. Below

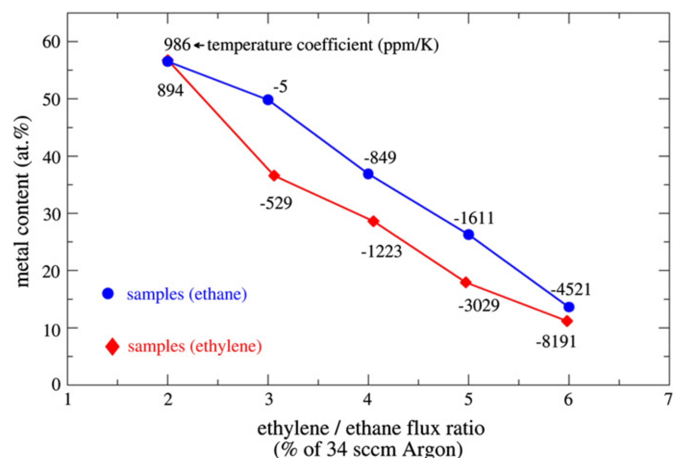

Fig. 2. Measured concentration of nickel in the films as a function of the ethylene (ethane) flux ratio in the plasma process. The TCR value is indicated at each measuring point.

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