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Electrical and magnetic properties of electrodeposited nickel incorporated diamond-like carbon thin films

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ABSTRACT

Nanocomposite diamond-like carbon (DLC) thin films have been synthesized by incorporating nickel (Ni) nanoparticles in DLC matrix with varying concentration of nickel. DLC and Ni-DLC thin films have been deposited on ITO coated glass substrates employing low voltage electrodeposition method. Electrical properties of the samples were studied by measuring current–voltage characteristics and dielectric properties. The current approaches toward an ohmic behavior with metal addition. This tendency of increasing ohmicity is enhanced with increase in dilution of the electrolyte. The conductivity increases with Ni addition and interestingly it continues to increase with dilution of Ni concentration in the electrolyte in the range of our study. Magnetic properties for DLC and Ni-DLC thin film samples were examined by electron paramagnetic resonance (EPR) measurements and Super Conducting Quantum Interference Device (SQUID) measurements. *g*-Value for DLC is 2.074, whereas it decreases to 2.055 with Ni addition in the electrolyte. This decrement arises from the increased sp^2 content in DLC matrix. The magnetic moment vs. magnetic field (m–H) curves of Ni-DLC indicate superparamagnetic behavior which may be due to ferromagnetic contribution from the incorporated nickel nanoparticles in the DLC matrix. The ZFC curve of Ni-DLC after the blocking temperature shows a combined contribution of ferromagnetic, superparamagnetic and paramagnetic nature of the materials persisting up to 300 K.

1. Introduction

The astounding euphoria that surrounds diamond-like carbon (DLC) thin films is phenomenal even after years of its fabrication and can be credited to its astonishingly splendid properties like superb hardness, excellent wear resistance, high chemical inertness, good optical transparency, exceptional electrical insulation and thermal conductivity [1–4] making them marvelously suitable in structural, mechanical, electrical, optical, chemical and acoustic applications [5–7]. DLC films have inherent problem of very high compressive stress which when accumulates to a certain level in the film, generates some severe problems like degradation of electrical and optical properties and peeling-off of the films from the substrate restricting its diverse applications [8,9]. However, it is expected that the addition of metals in the DLC film can create a two dimensional array of metal clusters within the carbon matrix improving the properties of DLC films by reducing compressive stress and increasing bonding strength thereby enhancing the adhesion of the film to the substrate. It has been established that in metal-DLC films, metal nanoclusters are formed and dispersed homogeneously in the amorphous carbon matrix; as DLC with its tunable band gap appears to be a suitable host matrix for inclusion of metal atoms in nanocrystalline form thus preserving their individuality and modifying the properties of the film [10–12]. Various groups have strived to deposit metal incorporated DLC films from conventional techniques such as PVD, CVD etc. but a successful and homogeneous distribution of metal nanoparticles is continued to be a challenge. Some groups have investigated and reported successful and consistent distribution of nanoparticles of noble metals into the DLC matrix by a chemical route – electrodeposition process [13–15].

A number of groups have made investigations on the effect of nickel incorporation in DLC thin films [16,17]. We have also reported the successful deposition of Ni-DLC thin films by electrodeposition technique and the consequent modification of various characteristics of the DLC films with nickel addition [18–20]. It is well established that despite having a modest band gap DLC films do not behave as typical semiconductors. Electrical properties of DLC films can be improved by adding metals, because metal addition decreases its resistivity on account of dopant induced

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graphitization. Thus with efficient doping and incorporation of metals in DLC, its electrical properties can be appropriately varied from insulating to highly conducting state. Some researchers have shown that the conductivity of the DLC film varies with the amount of the incorporated metals in it [21,22]. Omer et al. [23,24] investigated the effects of iodine doping on the electrical and optical properties of diamond-like carbon (DLC) thin films grown by microwave surface wave plasma chemical vapor deposition at low temperature. They studied electrical conductivity of DLC films deposited on glass substrates by the measurements of *I–V* characteristics before and after indium doping.

The microstructure of DLC is complicated due to the presence of both σ and π states; also the availability of large density of defect states in the optical band gap has been a limiting factor in its effective use in device application [21,25,26]. Such electronic properties render DLC, more precisely metal-DLC to be potentially attractive material for electronic and optoelectronic applications. One such probable application is the use of metal-DLC as a cathode material for thin film field emission displays. The dielectric properties of the material are associated to its composition and structure [27–29]. Hence the study of dielectric properties of DLC films is practically important as they provide greater insight into its distinctive material characteristics. Though DLC and metal-DLC (Me-DLC) films have significant potential applications [1–7] still there have been relatively few reports on the dielectric properties of the films where majority of studies are based on a particular frequency which make correlation of results difficult. Also we did not find any report on the studies of dielectric properties of electrodeposited Ni-DLC thin films till date. Romanko et al. [27] discussed the effect of deposition parameters on the dielectric properties of amorphous hydrogenated carbon films deposited from RF-discharge plasma in high frequency range. Huang et al. [30] investigated the dielectric properties of a set of molybdenum (Mo)-containing DLC films deposited by electron cyclotron resonance chemical vapor deposition (ECR-CVD). They demonstrated that the film permittivity increased significantly by the introduction of Mo, and a sharp decrease in permittivity occurred at low frequencies. The study of dielectric properties of DLC and Me-DLC films are scientifically important as they provide greater insight into material characteristics and their dependence on frequency is practically useful due to their potential usage in integrated circuit [31].

In spite of the reported high spin concentrations in the range of 10^{19}–10^{21} spins cm^{-3} of the amorphous carbon films such as DLC [32–35], the information on the nature of the paramagnetic centers in these films and their structural environment is still very limited. Since all the forms of amorphous carbon films contain defects which are believed to affect its ability to dope the material. It is therefore of interest to recognize these defects. Electron paramagnetic resonance (EPR) can impart some information about paramagnetic defects. Hence the paramagnetic properties of the Ni-DLC thin films have been investigated here by EPR measurements. Although few groups have studied magnetic properties of DLC and metal doped DLCs but we are not aware of any magnetic characterizations of electrodeposited Ni-DLC thin films yet. Colon Santana et al. [36] reported magnetism studies of chromium (Cr) doped DLC thin films synthesized by plasma assisted vapor deposition method. They found that Cr doped DLC thin films exhibited ferromagnetic property at very low temperatures, whereas Cr_3C_2 clusters appeared to be antiferromagnetic. Saito et al. [37] reported magnetization studies of DLC produced by RF plasma-enhanced CVD method using vibrating sample magnetometer (VSM). They established that magnetization of DLC film was diamagnetic when it was deposited on a silicon substrate. But the films deposited on a stainless steel substrate showed ferromagnetic behavior. It has been a usual concept that organic materials like DLC can exhibit ferromagnetic behavior. Experimental results encouraged various groups to explore further organic materials as magnetic materials. Hayashi et al. [38] were the first to deposit Co–C films using ion beam sputtering. Delaunay et al. [39] deposited samples with different Co contents by the same method. Wang [40] conducted several investigations on Co–C magnetic films produced by pulsed filtered vacuum arc deposition [41]. In another report [42] it was revealed that the as deposited films were soft ferromagnets. Host et al. [43] reported the dependence of room temperature saturation magnetization, remnant magnetization and coercive field of graphite encapsulated Ni and Co particles on annealing temperature. Tian et al. [44] reported magneto-resistance measurements on Fe-doped amorphous carbon films prepared by pulsed laser deposition method. Sedlackova et al. [45] reported the correlation of structural electronic and mechanical properties of carbon–nickel composite thin films with variation of deposition temperature where the films were grown by dc magnetron sputtering.

Highly sensitive SQUID measurements can be used to find out ferromagnetism in DLC. Nickel is one of the well-known ferromagnetic metals. Here we also aim to study the magnetic properties of our magnetic metal particle incorporated Ni-DLC thin films for its potential magnetic applications. Ni-DLC films may find usage in optoelectronics and in magnetic devices [30,31,36,37]. It is possible to control the size of incorporated metal particles inside DLC matrix [36,37]. We expect that the magnetic properties of the films can be tailored by manipulation of the size of metal particles. Accordingly the films may be superparamagnetic at smaller particle size and ferromagnetic at larger particle size. The challenge lies in how big the metal particles can be made in nanoscale. Thus, it would be interesting to employ metal-DLC thin films for production of magnetic storage device such as hard disks combining both the active magnetic and protective layers in a single coating. The role of DLC films as a host matrix in tailoring the band gap for various optical device applications have been discussed extensively, but its possible applications as a DMS (dilute magnetic semiconductors) material has not been explored systematically. Moreover DLC matrix would provide a versatile opportunity in tailoring the dielectric property of the host matrix by varying relative amount of sp^2 and sp^3 bonded carbon in the DLC film. The above issues and aspects prompted us to take up the investigations which have been dealt in this paper, especially on the exploration of conducting, dielectric and paramagnetic behavior of electrodeposited Ni-DLC nanocomposite thin films with varied Ni concentration and demonstration of ferromagnetic behavior in Ni-DLC film at low temperature [46].

2. Experimental details

The nanocomposite thin films of DLC and Ni-DLC were synthesized on ITO coated glass substrates at an optimum voltage of 2.47 V at room temperature for 40 min in an electrodeposition system [18–20]. DLC thin films were deposited at a fixed volume percent (1%, v/v) of an aqueous solution of 0.17 M acetic acid (CH_3COOH) and deionized water. The incorporation of nickel was carried out by adding controlled amount of M/100 nickel acetate into the electrolytic bath (1%, v/v, of acetic acid in deionized water). Films were annealed at 80 °C in air for 20 min and stored in a clean and dry environment. Thin film samples, designated as (S1–S3) of varying Ni content were grown from electrolytes having Ni ions in increasing order as shown in Table 1.

The microstructural, electrical and magnetic properties of the annealed DLC and Ni-DLC thin films were studied by performing transmission electron microscopy (TEM), current–voltage (*I–V*) characteristic measurements, dielectric measurements, electron paramagnetic resonance (EPR) spectroscopy and Superconducting Quantum Interference Device (SQUID) measurements.