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Investigation of properties of Cu containing DLC films produced by PECVD process

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ABSTRACT

Copper containing diamond like carbon (Cu-DLC) thin films were deposited on various substrates at a base pressure of 1×10^{-3} Torr using a hybrid system involving DC-sputtering and radio frequency-plasma enhanced chemical vapor deposition (RF-PECVD) techniques. The compressive residual stresses of these films were found to be considerably lower, varying between 0.7 and 0.94 GPa and Cu incorporation in these films improve their conductivity significantly. Their structural properties were studied by Raman spectroscopy, atomic force microscopy, scanning electron microscopy, X-ray photoelectron spectroscopy and X-ray diffraction techniques that clearly revealed the presence of Cu in the DLC structure. Raman analysis yields that Cu incorporation in DLC enhances the graphite-like sp^2 bonding. However, the sp^2 bonding was found to continuously reduce with the increasing C_2H_2 gas pressure, this may be due to reduction of Cu nanocrystal at the higher pressure. FTIR results inferred various bonding states of carbon with carbon, hydrogen and oxygen. In addition, hydrogen content and sp^3 and sp^2 fractions in different Cu-DLC films were also estimated by FTIR spectra and were correlated with stress, electrical, optical and nano-mechanical properties of Cu-DLC films. The effect of indentation load (4–10 mN) on nano-mechanical properties of these films was also explored.

1. Introduction

Diamond like carbon (DLC) or hard hydrogenated amorphous carbon (a-C:H) is recognized as a promising alternative material for various applications such as cutting tools, wear and hard disk due to its high hardness, low friction coefficient, high thermal conductivity and very high optical transparency in infrared (IR) region [1–7]. The ability to tune various hybridizations states of carbon in DLC by changing process parameters has led recent research into this material for exploring explore its electronic and photovoltaic properties [8–11]. However, poor adhesion of DLC films with the substrate due to high compressive residual stress restricts its widespread applications [12,13]. It should be noted that the adhesion of DLC films with substrates can be improved by doping of silicon, nitrogen and fluorine (Si, N, F), though at the expense of some of their other properties [14–16]. In contrast, the incorporation of metals into DLC films is an alternative method that improves the adhesion of these films with substrate without affecting their other properties [17–19]. Moreover, lower conductivity in DLC films, which restricts its potential electronic application, can also be resolved by incorporating metal in DLC matrix (as its incorporation in DLC structure may improve the transport properties). Although some reports pertaining to decrease of residual stress with metal addition have already been investigated, there is a lack of literature on the enhancement of transport properties with incorporation of Cu in DLC film.

In this paper, the reduction in stress and improvement in transport properties of DLC films due to incorporation of Cu in DLC matrix have been explored. In addition, measured conductivity of different Cu-DLC films are correlated with hydrogen content and C–H based sp^3 and sp^2 fractions. Their structural, morphological and nano-mechanical properties have also been investigated by X-ray photoelectron microscopy (XPS), Raman spectroscopy, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), atomic force microscopy (AFM) and nanoindentation measurements were performed.

2. Experimental details

Cu-DLC films were deposited on various substrates using a combined DC sputtering and RF-PECVD hybrid system. The schematic representation of the deposition unit used for the growth of Cu-DLC films is shown in Fig. 1. Roots and rotary pumps

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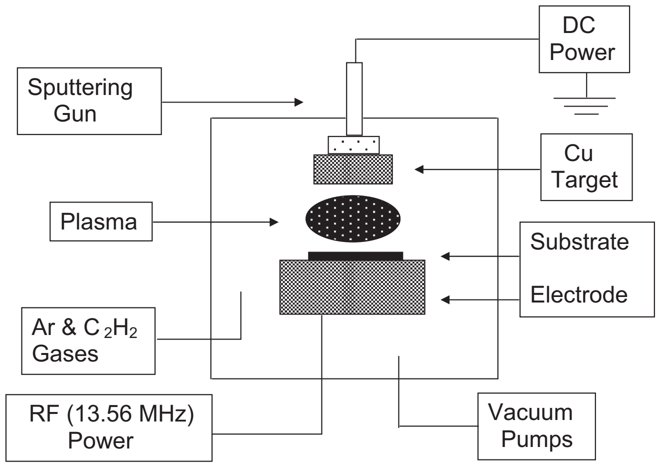

Fig. 1. Schematic representation of deposition unit used for the growth of Cu-DLC films.

Table 1
Process parameters for the growth of Cu-DLC films.

Samples	Ar pre. (mTorr)	DC power (W)	C_2H_2 pre. (mTorr)	Negative self bias (V)	Thickness (nm)
A	150	8	25	100	151
B	150	8	50	100	159
C	150	8	75	100	168

were used to obtain base vacuum of 1×10^{-3} Torr. Sputtering gun, having Cu target and attached with DC power supply, was fixed on the top of process chamber. The RF (13.56 MHz) power supply was attached to the substrate electrode. Argon (Ar) and acetylene (C_2H_2) were used as working gases. The Cu target of 2 in. diameter was kept 5 cm apart from the substrate to sputter Cu by energetic Ar ions. The substrates used in the present study were n-type silicon wafer ⟨100⟩, both side polished p-type silicon wafer, corning 7059 glass and stainless steel. The substrates were cleaned in Ar plasma for 10 min prior to the film deposition for avoiding moisture effect from the surface. Cu-DLC films were deposited at fixed negative self bias of 100 V with varying C_2H_2 gas pressures of 25, 50 and 75 mTorr (samples A, B and C, respectively). DC power of 8 W and Ar gas pressure of 150 mTorr were kept fixed in all the runs and were applied to sputtering unit for sputtering of Cu particles. Deposition parameter used for the growth of Cu-DLC films is summarized in Table 1.

Thickness of Cu-DLC films were estimated by Taylor–Hobson talystep instrument. Residual stresses in these films deposited on silicon wafer were determined from the change in the radius of curvature of the wafer, before and after deposition, using 500TC temperature controlled film stress measurement system (M/s FSM Frontier Semiconductor, USA). The substrate curvature method generally relies on the Stoney formula relating the film average stress (S) to the substrate curvature under the assumption that the film is much thinner than the underlying substrate. The Stoney formula, which was used to estimate S is given in Eq. (1)

$$S=\frac{E_s d_s^{\,2}}{6(1-v_s)d_f}\left(\frac{1}{R_f}-\frac{1}{R_0}\right) \tag{1}$$

where E_s, v_s, d_f and d_s are Elastic modulus, Poisson ratio, thickness of the film and the thickness of the substrate, respectively, and R_0 and R_f are the radii of substrate curvature before and after film deposition, respectively. Temperature dependent conductivity measurements were carried out using Keithley 610C solid state electro-meter in coplanar configuration with gap of 0.078 cm where aluminum was evaporated in a vacuum better than 10^{-5} Torr. AFM measurements were performed by Nanoscope Veeco V (USA) instruments to analyze surface morphology and surface roughness of the films. Morphologies of the deposited films were studied also by SEM, model: LEO Electron Microscope 7060. An XPS spectrum was obtained from Perkin Elmer 1257 instrument by X-ray radiation of MgK_α of 1253.6 eV to analyze the composition and structural properties of the films. XRD measurement in the 2θ of 20–60° was carried out by Rigaku Miniflex II diffractometer to investigate the crystallinity and phase composition of the films. Transmission measurement was carried out in the UV and near IR range by Shimadzu UV-Vis 1601 instrument. FTIR measurement was carried out by Perkin Elmer Spectrum Bx instrument in the wave number between 2700 and 3700 cm^{-1}. Nanoindentation measurement was performed by using IBIS nanoindentation, Fisher-Cripps Laboratories Pvt. Limited, Australia under applying maximum indentation loads of 4, 5 and 10 mN.

3. Results and discussion

3.1. Film thickness and deposition rate

Thickness of Cu-DLC films grown at C_2H_2 gas pressures of 25, 50 and 75 mTorr was found to be 151, 159 and 168 nm, respectively. Since depositions were performed for different timings at different C_2H_2 gas pressures, the deposition rates were also calculated in order to clarify the role of C_2H_2 gas pressures on thickness. The deposition rates for Cu-DLC films at different C_2H_2 gas pressures of 25, 50 and 75 mTorr were found to be 1.21 nm/s, 1.77 nm/s and 2.3 nm/s, respectively. Therefore, enhanced C_2H_2 gas pressures leads to higher deposition rates.

3.2. AFM and SEM analyses

Atomic force microscopy (AFM) and scanning electron microscopy (SEM) analyses were carried out to investigate the surface morphology of the films. Typical AFM and SEM micrographs of Cu-DLC film deposited at C_2H_2 gas pressure of 25 mTorr are shown in Fig. 2(a) and (b), respectively. AFM micrograph clearly shows the spreading of nanocrystalline Cu particles in amorphous DLC matrix. Pauleau et al. [20] and Gerhard et al. [21,22] have also reported the Cu nanocrystal formation in DLC matrix. The mean roughness R_a of Cu-DLC film deposited at C_2H_2 gas pressure of 25 mTorr was found to be as low as 0.22 nm. Observed SEM micrograph also followed similar surface morphology and showed the presence of nanocrystalline Cu particles in amorphous DLC matrix. Recently, Mousinho et al. [23] have also reported the growth of nanocrystalline structure in amorphous DLC matrix. However, instead of incorporation of foreign elements in DLC films they performed some pretreatments on substrates and modified their surface topography by diamond, graphite powders and wet chemical, plasma etchings before the DLC deposition. After deposition they obtained different nanocrystalline DLC films whose surface feature was dependent on the pretreated surface features of the substrate. They had observed high sp^2 bonding with graphite powder modified substrate, though in contrast we obtained high sp^2 bonding by Cu incorporation.

3.3. XPS analysis

X-ray photoelectron spectroscopy (XPS) is a very reliable technique to investigate chemical composition as well as bonding of the structures. XPS spectrum was recorded for Cu-DLC film deposited at C_2H_2 gas pressure of 25 mTorr (sample A). Three different core level