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Enhanced electron field emission of Cu implanted microcrystalline diamond films after annealing

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ABSTRACT

Effects of Cu ions implantation on the structure and electron field emission (EFE) properties of microcrystalline diamond (MCD) films were investigated. The MCD films implanted with Cu ions at a fluence of 1.0×10^{17} ions/cm^2 and subsequent annealing in N_2 atmosphere at 600 °C for 2 h achieved good electrical conductivity with lower surface resistance of 0.1301 Ω/sq, high carrier concentration of 7.621×10^{18} cm^{-3} and hall mobility of 62 cm^2 V^{-1}s^{-1}. Our results show that Cu nanoparticles can be formed in surface of MCD films after Cu ion implantation and annealing, which induced the formation of graphitic phases during annealing process. Consequently, the presence of Cu nanoparticles and graphitic phase formed conduction channels for efficient electron transport, ensuing better electron field emission (EFE) properties for Cu ion implanted/annealed MCD film with low turn-on field of 2.234 V/μm and high EFE current density of 28.560 μA/cm^2 at an applied field of 4.172 V/μm.

1. Introduction

Diamond has attracted attention and is known as a candidate optimal material on the electron field emission due to its negative electron affinity characteristics and low effective work function [1–3]. Moreover, diamond has received considerable attention owing to their interesting properties, e.g., the highest thermal conductivity and hardness among all known materials, wide band gap, high radiation resistance, good chemical and temperature stabilities. These appealing properties make diamond an ideal substrate to work in severe environments, e.g., high temperature, high radiation flux, etc [4]. Consequently, the potential and the application of diamond-like materials for the fabrication of cold cathode emitting devices require the films to be conductive.

Researchers have studied the effects on chemical vapor deposition (CVD) diamond films with the increasing sp^2-bonded regions in the grain boundary area and found out that sp^2-bonded carbon within the CVD diamond films can be thought of as a conduction promoter, particularly if the sp^2 bonds form interconnected networks [5–10]. Recently, implantation technology has been widely used to manufacture semiconductor devices and in many fundamental researches of materials due to their excellent advantages on accurate controllability, superfine processing and no thermal limitation during "element doping". Ion implantation for diamond films results in defect creation (substitution, interstitial and vacancies creation), doping, re-crystallization and other significative phenomena, depending on the ion beam parameters such as ion implantation dose and the energy loss of ions in materials [11]. Moreover, the C-C and C-H bonds can be broken in the ion implantation process to form sp^2 carbon under controlled manner, which make ion implantation an efficient and reliable way to control the proportion of sp^2 bonds in the materials [12]. Also, Cu has been utilized for synthesizing the graphene in chemical vapor deposition process, implying that Cu has some degree of solubility to carbon species and catalytically induces the formation of sp^2-bonded carbons [13]. Therefore, it is desirable to modify the electrical properties of MCD films using Cu ion implantation.

In this context, Cu ions were implanted in MCD films followed by annealing at 600 °C to obtain high electrical conductivity and better EFE properties of the MCD films. The modifications to the microstructure and electrical properties of MCD films due to Cu ion implantation/annealing process were investigated in detail using

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several technologies. We observed that the possible mechanism of high electrical conductivity and improved EFE properties of MCD films is the formation of Cu nanoparticles (Cu NPs) and graphite phases in the films.

2. Experimental

The microcrystalline diamond (MCD) films were grown on n-type silicon substrates by a home-made microwave plasma chemical vapor deposition (MPCVD) apparatus. The substrates were cleaned by ultrasonic cleaning in acetone and methanol about 10 min respectively to degrease the contaminants on the surface. Then the substrates were ultrasonicated in a methanol containing diamond powers (about 5 nm in size) for 45 min to facilitate the nucleation and achieve a continuous thin film. The MCD films were grown in H_2 (98.6%)/CH_4 (1.4%) plasma excited by microwave power 7 kW with the total gas flow rate 406 sccm at a total pressure 10^5 torr for 10 h. Its temperature was estimated to be around 850 °C during the growth process of MCD films on account of the bombardment of the plasma species, which was monitored by a thermocouple embedded in the stainless steel substrate holder. Cu ion implantation was carried out in a metal vapor vacuum arc (MEVVA) implanter at room temperature at a fluence of 1×10^{17} ions/cm^2 with the implantation energy of 100 keV. In order to avoid significant local temperature rise during the beam heating, the ion beam current was maintained at 5 μA/cm^2 in the whole process of Cu ion implantation. Samples were placed in the vacuum tubular furnace with the instrument model OTF-1200X after Cu ion implantation and subjected to furnace annealing in N_2 atmosphere at 600 °C for 2 h. The pristine microcrystalline diamond film is designated as “pristine-MCD”, whereas the Cu-implanted diamond film is designated as “Cu-MCD”, the sample via Cu ion implanted/annealed at 600 °C for 2 h is designated as Cu-MCD-600 °C. To understand the factors resulting in more pronounced improvement on the EFE properties for MCD film after ion implantation/annealing, the phase transformation and the formation of sp^2 carbon for MCD films were further investigated by several measurements as follows.

Hall effects measurements by in Van der Pauw configuration were performed at room temperature on the Accent HL5500 Hall System to observe the conducting behavior of the films. Depth profiles of Cu ions distribution in MCD film were calculated using SRIM-2008 code. The electron field emission (EFE) measurements were performed on a high vacuum field emission system with a tunable parallel plate set-up, including two parts, an indium tin oxide (ITO)-coated glass was used as anode, and the MCD sample was used as cathode. The distance between anode probe and cathode diamond films is 150 μm, which was controlled using an adjustable micrometer. The current density versus electrical field (J-E) characteristics were measured by Keithley 237. Grazing incidence X-ray diffraction (GXRD) measurements were made using Cu Kαline (λ = 0.154 nm) with an incident angle of 0.3° to identify the phase composition. The surface chemical bonding characteristics of MCD films were investigated by X-ray photoelectron microscopy (XPS; K-Alpha). Field emission scanning electron microscope (FESEM; JSM-7001F\QX200) operated at an electron energy of 10 keV and an atomic force microscope (AFM; SPA-300HV) worked in the contact mode with a scanning area 2 × 2 μm^2 were employed to investigate the surface morphology of the MCD films. Crystal quality of MCD films before and after Cu ion implantation were investigated by Raman spectroscopy (Raman; RENISHAW InVia) using 532 nm argon laser beam.

3. Results and discussion

Typical depth distributions of Cu ions in MCD films calculated using SRIM-2008 [14] are presented in Fig. 1(a–b). The Cu ions are implanted into MCD films to a depth of about 80 nm with peak concentration located at around 40 nm beneath the surface, and the 100 keV Cu ions have a longitudinal range of 44.4 nm in diamond with longitudinal straggling of 11.5 nm. Heavy ion implantation at low energy will result in sputtering erosion of the substrate surface, the fluence dependent depth distribution function of implants in a substrate can be expressed as [15]:

$$G_{(Z)} = \frac{N}{2Y}\left[\mathrm{erf}\left(\frac{z - R_p + \frac{\Phi Y}{N}}{\sqrt{2}\Delta R_p}\right) - \left(\mathrm{erf}\left(\frac{z - R}{\sqrt{2}\Delta R_p}\right)\right)\right] \quad (1)$$

where z is the depth coordinate with respect to the surface, N is the atomic density of the substrate, Y is the sputtering yield, Φ is the ion fluence, R_p is the projected range of ions, ΔR_p is the range straggling related to R_p, and erf is the error function. By using Eq. (1) and calculating Cu ion implanted distribution as a function of energy after taking into account the sputtering yield, the concentration profile of MCD film is given in Fig. 1(c), where R_p, ΔR_p, and Y could be obtained by SRIM. Comparation the two curves, one can clear see that the sputtered surface layer induced by Cu ion implantation is little. Therefore, Cu ions merely cause damage in near surface region of diamond films keeping the high ‘structural’ quality of the bulk MCD films [16,17].

Comparison on electrical resistivity and hall mobility for MCD films are given in Table 1. The electrical properties of MCD films have been changed before and after Cu ion implantation/annealing. The pristine-MCD film shows the characteristics of the high surface resistance 86.26 Ω/sq and low carrier concentration. For Cu-MCD sample, the surface resistance decreases with its carrier concentration increase, however, the crystal lattice distortion in the diamond caused by high dose Cu ion implantation will hinder electron transportation and migration, which result in the hall mobility decrease. After 600 °C annealing in N_2 atmosphere for 2 h, the surface resistance decreases to 0.1301 Ω/sq, carrier concentration increases to 7.621 × 10^{18} cm^{-3}, and hall mobility reaches to 62 cm^2 V^{-1}s^{-1}. It can be concluded that the Cu ion implantation/annealing can improve the electrical performance of the MCD films.

Fig. 2 depicts the effects of Cu ions implantation/annealing on the electron field emission (EFE) characteristics of MCD films. The data are analysed by applying Fowler-Nordheim (F-N) equation [18] and the F-N plots are shown as the insets in this figure, where the turn-on field is defined as the field that provides an overall current of 1 μA. It is well known that the FN model was developed to explain the emission from metal. The details of the field emission parameters, such as turn-on field (E_0) and EFE current density (J_e) are given in Table 2. Although the diamond plane (111) has negative electron affinity [19], its inhomogeneity and high resistance hindered the EFE performance. A reduction in the turn-on field is observed for MCD films before and after ions implantation, more importantly, a large reduction can be seen after annealing. For Cu-MCD-600 °C, the E_0 dramatically decreased to 2.234 V/μm, and J_e increased to 28.560 μA/cm^2 with the applied field at 4.172 V/μm. The Cu-implanted/annealed processing enhanced the EFE properties of the MCD films, which are in good accordance with Hall effects measurements.

Fig. 3 depicts the GXRD pattern of the MCD film before and after implanted with 100 keV Cu ions at a fluence of 1×10^{17} ions/cm^2 and followed by annealing in N_2 atmosphere at 600 °C for 2 h. As shown in Fig. 3, GXRD presents a strong sharp diffraction peak situated at about 43.92° for pristine-MCD, which can be assigned to