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AC behavior of intrinsic nanocrystalline diamond films

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Abstract

Nanocrystalline diamond was prepared by hot filament assisted chemical vapor deposition technique. The nanometer sized dimension of diamond grains was determined by X-ray line broadening. AC electrical response of deposits, constituted by well formed diamond grains, was studied by admittance spectroscopy at different temperatures. Grain boundary and grain surface were considered different regions able to influence differently the frequency dependent AC response. Observed variations in admittance spectra were attributed to a modification of the grain surface response as frequency and temperature rise. A semiconductor to metal-like transition was evidenced in admittance spectra increasing the frequency of applied signal at lower temperatures.

Keywords: AC measurements; Grain boundary; Admittance spectroscopy; Nanocrystalline diamond

1. Introduction

Today there is a growing interest in the size dependent transport properties of nanocrystalline diamond (NCD) produced by hydrogen-poor growth conditions. Usually, changes in electrical properties are linked to a band structure modification due to lattice spatial modulation, charge carriers quantum confinement and dominant contributions from largely defective and strained grain boundaries (GBs). In the case of indirect gap semiconductor nanostructures, the increase in forbidden energy gap, related to a conductivity decrease, is usually observed whereas semiconductors like CdS in nanosize regime exhibit an increase in conductivity in comparison with the bulk counterpart [1]. NCD is expected to have distorted sp^3 and dangling bonds on the grain surface, as a consequence of the small curvature radius, which may result in surface compressive and tensile stressed domains decreasing the deposition temperature. Such defects may cause a pronounced surface conductivity if compared with the insulating nature of diamond grains. Therefore, due to the morphology of nanosized diamond, presence of different conductivity contributions is expected. Bataineh and Reinhard [2] for example evidenced transport at GBs as the main contribution to the current flow at room temperature and the conductivity over the grain surfaces as an additional channel parallel to the GBs frequency dependent transport of finer-grain diamond samples. Ye et al. [3] evidenced a dielectric transition in the response of nanostructured diamond films in the range 50–500 °C. These authors concluded that nanostructured diamond films show a transition from grain interior dominating to grain boundary dominating conductivity at about 250 °C. A change of crystal field caused by the thermal expansion or by surface bond contraction has been proposed as responsible for the observed dielectric transition in this material.

Since current transport in such a system is mainly sustained by hopping motion of carriers among disordered regions, the Correlated Barrier Hopping (CBH) model is usually employed for analyzing the electrical conductivity data of materials which exhibit defect dependent conductivity [4]. Such model will be used to discuss the AC response of thin NCD films prepared by hot filament assisted CVD technique on silicon.

2. Experiment

A custom hot filament assisted CVD reactor was used to prepare NCD specimens with thickness in the micrometer

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range. Polished (100) intrinsic Si wafer was used as substrate. Bias Enhanced Nucleation (BEN) process was performed with a two grids technique to enhance the nucleation density. According to the conditions optimized in a previous work [5], the BEN process lasted 60 min keeping constant the following parameters: H_2:CH_4=100:2, Tsub=600 °C, Tfil=2100 °C, Vbias=240 V, Jbias=5 mA/cm^2. Nanocrystalline diamond films were then grown with a modification of the gas mixture to Ar:H_2:CH_4=100:30:1.

The AC response was analyzed as a function of temperature in the 0.01 Hz–30 kHz range by using a Solartron 1250 frequency response analyzer equipped with a 1296 dielectric interface and a 12961 dielectric reference module, whereas a HP4192A LF impedance analyzer was used in the 30 kHz–10 MHz range. Admittance as a function of frequency was then measured employing a two probe method using an AC amplitude of 1 Vpp without DC bias. Silver contacts deposited through a shadow mask were then realized by thermal evaporation. A preliminary annealing at 600 K was performed aimed to obtain ohmic and symmetric *I–V* characteristics. The measurements have been carried out under vacuum at each programmed temperature in the range 300–600 K with an accuracy of ±1 K.

3. Results and discussion

3.1. Morphology and structure

Nanocrystalline structure of the specimen under study has been probed by X-ray diffraction analysis using a Bragg–Brentano geometry. Recorded intensities in the range 38–50° 2θ are shown in Fig. 1. Counts have been measured each at 0.01° with a preset time of 80 s. No corrections have been applied for thin film and Lorentz-Polarization. Line broadening analysis of diamond (111) contribution at 44.17° 2θ led to a grain size of 30± 5 nm. Noticeable is the asymmetry at low angle addressing a distribution of grains. Besides, Raman analysis of such specimen showed the presence of a small peak at approximately 1150 cm^{-1} usually associated with NCD. Furthermore, XPS energy loss region of the C(1s) core level shows the typical diamond surface and bulk plasmon peaks at 22 eV and 34 eV while any graphite contribution was absent. Details on these characterization results can be found elsewhere [6].

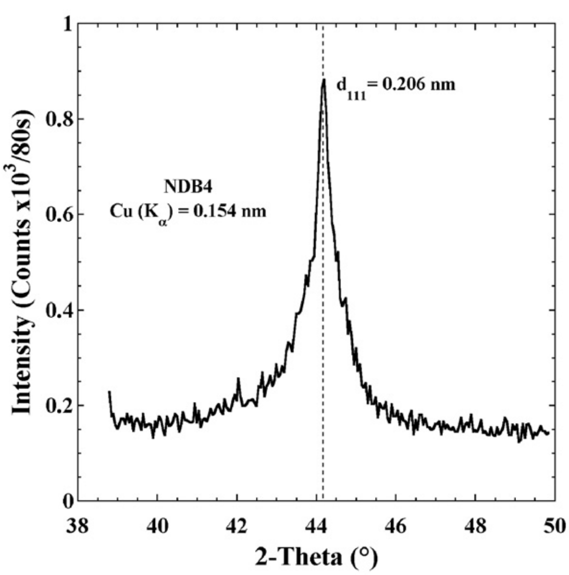

Fig. 1. X-ray diffraction spectrum of a 0.4 μm thick NCD specimen.

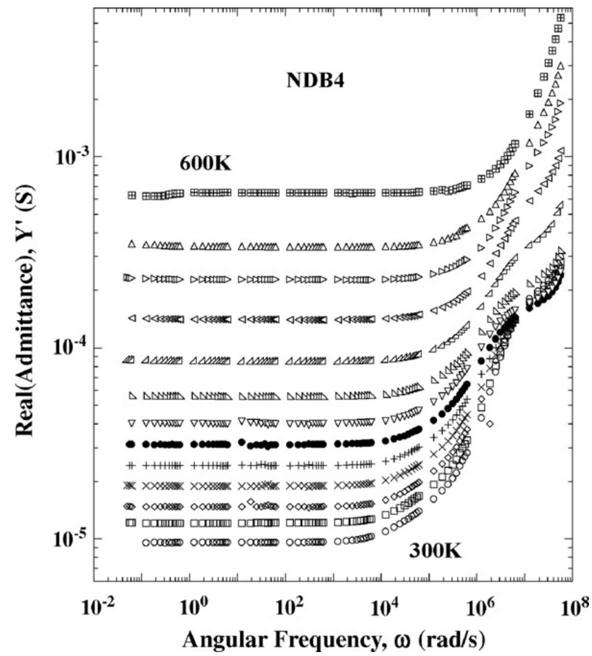

Fig. 2. Real part of the admittance at different temperatures of the sample in Fig. 1. Temperature step is 25 K. Symbol (●) corresponds to the measure at 425 K.

3.2. Electrical characterization

In the framework of the CBH model two different types of charge carriers movements are considered: i) inter-well hopping involving the jump of a carrier, located in a defect potential well, in an adjacent defect potential well; ii) hopping of charge carriers between sites within the same defect potential well constituting intra-well hopping. In the presence of a DC bias, the probability of occurrence of intra-well hopping is zero and all charge carriers take part in inter-well hopping, resulting in pure DC conduction. However, in the presence of an AC signal, both the above mentioned charge transfer mechanisms do have a finite probability of occurrence, their relative probabilities being dependent on charge carriers energy, their concentration, frequency of the applied signal, mean site separation, depth and extent of potential wells percolation. Hence, the measured real part of admittance $Y'(\omega,T)$ is constituted by a frequency independent DC component, Y_{DC} (due to inter-well hopping), and a frequency dependent AC component, Y_{AC} (due to intra-well hopping), i.e. $Y'(\omega,T)=Y_{DC}+Y_{AC}$. Experimental $Y'(\omega,T)$ curves are reported in Fig. 2 versus angular frequency, ω, and temperature, T. Real part of admittance is found independent of frequency below 10^4 rad/s. This low-frequency region corresponds to DC conductivity where the inter-well hopping completely dominates over intra-well hopping associated with