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Low temperature electron spin resonance investigation of ultrananocrystalline diamond films as a function of nitrogen content

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Abstract

We have investigated the room and low temperature ESR signals in a series of ultrananocrystalline diamond films grown with different N_2 enrichments in the gas phase. We have found that exchange interaction is playing the major role in spin–spin interaction and determines the linewidths. The relatively high values of spin–lattice relaxation and other features of the ESR signals show that the ESR active centers are sitting in the grain boundaries' regions.

Keywords: Nanocrystalline diamond; Defects; Grain boundaries

1. Introduction

Nanocrystalline diamond films have become increasingly important in the field of diamond research due to their low cost and their wide scope of potential applications [1]. Of particular importance for electrochemical and electrical applications is the control of conductivity. Ultrananocrystalline diamond can be rendered n-type by the addition of nitrogen in the gas phase during deposition [2]. This conductivity is not due to doping, but rather to the manipulation of the nanostructure, resulting in broad grain boundary regions [3]. Optical measurements have shown the origin of conductivity to be related to mid-gap states due to π bonding [4] and has transport characteristics of a low dimensional disordered metal [5]. Although this conductivity mechanism is not true doping, it has uses for electrodes and devices such as high temperature heterostructures [6].

Electron spin resonance investigation is an analysis commonly used in semiconductor to investigate recombination centers, as it is sensitive to single occupied level states sitting in the gap between extended states bands. However, in amorphous carbon based materials the presence of photoconductivity even at high spin density levels (over 10^{20} spins/cm^3 [7]) shows that ESR active states are not necessarily recombination centers. It has been shown that mid-gap states due to π bonding in sp^2 coordinated clusters are responsible for ESR signal in amorphous carbons [8].

In this paper we report about ESR analysis of a series of N-enriched UNCD films at room and low temperature. We have investigated also the relaxation behavior of the excited spins. Although the identification of ESR active centers with delocalized π states belonging to sp^2-regions or sp^3 dangling bonds remains an open question, our results unambiguously show that the ESR active states are situated on grain boundaries. Such findings well agree with the results obtained on magnetoresistance [5].

2. Experimental

Microwave plasma enhanced CVD (MW-PECVD) system has been employed for the UNCD film preparation. An argon rich $Ar/N_2/CH_4$ gas mixture has been used as reactant gas for the MW discharges. The CH_4 flow rate was kept constant at 1 sccm, while the flow rate of argon was varied as increasing amounts of

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