Nitrogen-Doped Ultrananocrystalline Diamond/Amorphous Carbon Composited films Prepared by Pulsed Laser Deposition

サウサン サイード マルホーン アリヤミ

https://hdl.handle.net/2324/1398408

出版情報：九州大学, 2013, 博士（理学）, 課程博士
バージョン：

氏　　名：Sausan Said Marhoon Al-Riyami
（サウサン　サイード　マルホーン　アリヤミ）

論文題名：Nitrogen-Doped Ultrananocrystalline Diamond/Amorphous Carbon Composited films Prepared by Pulsed Laser Deposition
(レーザーアブレーション法による窒素ドープ超ナノ微結晶ダイヤモンド/アモルファスカーボン混相膜の作製とその構造と電気特性)

区　　分：甲

論 文 内 容 の 要 旨

Over the last two decades ultrananocrystalline diamond (UNCD)/hydrogenated amorphous (a-C:H) composite (UNCD/a-C:H) films, which are comprised of UNCD crystallites with diameter less than 10 nm and an a-C:H matrix, received much attention due to its unique electrical and mechanical properties. The preparation has mainly been conducted by chemical vapor deposition (CVD). While n-type conduction is extremely difficult to be formed for poly- and single-crystalline diamond, a few group has reported that nitrogen can acts as a candidate dopant for forming n-type UNCD/a-C:H. Several years ago, our laboratory succeeded in forming undoped and p-type boron-doped UNCD/a-C:H films by pulsed laser deposition (PLD). Hitherto, there have not been any research employing PLD for depositing nitrogen-doped UNCD/a-C:H films.

The main aim of this study is to prepare n-type ultrananocrystalline diamond (UNCD)/amorphous carbon (a-C) composite (UNCD/a-C) films in hydrogen and nitrogen mixed gas atmospheres using pulsed laser deposition for the first time to our knowledge in the research field of diamond. The production of n-type conduction accompanied by an enhancement in the electrical conductivity with increasing nitrogen content and their relation with the chemical bonding structure of films were studied in details. Since PLD makes possible the growth of nitrogenated films even in atmospheres excluding hydrogen, the incorporation effects of not only nitrogen atoms but also hydrogen atoms on the chemical bonding structure and electrical properties were widely discussed. Furthermore, the effects of nitrogenation on an improvement in the adhesion between films and metal substrates were studied and it was found that the enhanced adhesion is owing to sp^2 bonds formed by nitrogenation. Finally, heterojunction diodes comprising nitrogen-doped UNCD/a-C:H films and p-type silicon substrates were electrically evaluated as diodes. They exhibit a typical rectifying action and the results represent that the nitrogen-doped films act as an n-type semiconductor.

The above-mentioned results are discussed in several chapters as follows:

Chapter 1 overviews the background of researches on UNCD/a-C:H films. In particular, previous research results on the formation of n-type UNCD/a-C:H film by the incorporation of nitrogen atoms

and their structural and electrical evaluations are explained in details. In addition, the achievement of our group thus far are surveyed. Finally, the main aim of this study is explained.

Chapter 2 explains experimental methods that were employed for the preparation of UNCD/a-C:H films and the structural and electrical evaluations of the films.

Chapter 3 mainly discuss the incorporation effects of nitrogen atoms on the chemical bonding structure and electrical properties of the films. It was confirmed that n-type conduction is induced by nitrogen doping, accompanied by an enhancement in the electrical conductivity with increasing nitrogen content. On the basis of the results of the films deposited at various conditions such as in a nitrogen and hydrogen mixed gas atmosphere and a hydrogen-free nitrogen atmosphere, the roles of nitrogen and hydrogen in the film growth, chemical bonding structure, and electrical properties are discussed.

Chapter 4 discusses the electrical characterization of heterojunction diodes comprising nitrogen-doped UNCD/a-C:H films and p-type silicon substrates. From the current-voltage and capacitance-voltage measurements, the diode performances including the transport of carriers are discussed.

Chapter 5 focuses on the heavily doping of nitrogen. It was found that the disappearance of diamond grains in heavily doped films coincides with a sudden decrease in the electrical conductivity, which implies that the GBs have important roles in nitrogen doping for UNCD/a-C:H. This dramatic change in the film structure is discussed on the basis of the several spectroscopic measurements of the chemical bonding structure.

Chapter 6 reports the structures and electrical properties of nonhydrogenated nitrogen-doped UNCD/a-C films. Since it is impossible for the hydrogen-free films to be grown by CVD, this is the first report on hydrogen-free nitrogen-doped films, to our knowledge. They exhibited the similar electrical properties to hydrogenated films. On the other hand, it was found that C=C and C≡C bonds are preferentially formed instead of C-H bonds for hydrogenated films. In addition, the life time of photogenerated carriers is smaller than that of hydrogenated films, which might be because nitrogen atoms cannot sufficiently terminated dangling bonds that act as trap centers as compared with hydrogen atoms.

Chapter 7 discusses the enhancement of film adhesion with metallic substrates, concretely titanium substrates, by nitrogenation. From the chemical bonding structural analysis of the films, it was considered that the main reason might be the release of an internal stress by the enhanced formation of sp^2 and sp bonds.

Chapter 8 summarizes the above-mentioned experimental data and discussions and has a view of the future work after this.