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Review

Photochemistry and photo-electrochemistry on synthetic semiconducting diamond

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ABSTRACT

In this short review, we discuss the photo-relative properties, photochemical and photo-electrochemical applications of synthetic diamond materials. Synthetic diamond with semiconductive nature owns outstanding ideal properties of physics and chemistry, including high hardness, a wide bandgap, very high carrier mobility, excellent chemical stability, and inherent biocompatibility, which makes diamond promising candidate used in photochemistry and photo-electrochemistry. Diamond materials show p-type or n-type properties via doping of certain elements, which can be utilized in photo-involved chemistry for photo-synthesis, photo-catalysis, solar cells, photo-electronics, and surface modification.

Contents

Daibing Luo was born in 1977 in Sichuan China. He got his PhD from Technical Institute of Physics and Chemistry, Chinese Academy of Sciences at 2009. In 2015 he went to Tokyo University of Science as a research fellow associated with associate professor Kazuya Nakata under the guidance of Prof. Akira Fujishima. Now he works at Analytical & Testing Center, Sichuan University as an associate professor and carries out researches in the fields of crystal structure analysis, microplasma devices and inorganic materials.

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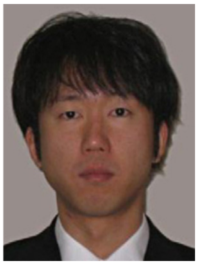

Kazuya Nakata was born in 1977 in Sapporo, Japan. He received his BSc (2000) from Shizuoka University, and his MSc (2002) and PhD (2005) in science from Tokyo Metropolitan University under the supervision of Professor Masahiro Yamashita. In 2005, he joined Tohoku University as a research fellow of the Japan Society for the Promotion of Science (JSPS), and then joined the Massachusetts Institute of Technology in 2006 as a JSPS research fellow. He has been a full-time researcher in the photocatalyst group at the Kanagawa Academy of Science and Technology (KAST) since December 2007. In September 2010, he also joined in the Organic Solar Cell Assessment Project at KAST. He has also been a visiting associate professor at the Tokyo University of Science since January 2011. In 2012, he received a Sano award for young scientists from the electrochemical society of Japan.

Akira Fujishima was born in 1942 in Tokyo, Japan. He received his BSc (1966) from the Yokohama National University, and his MSc (1968) and PhD (1971) in engineering from The University of Tokyo. He became a lecturer at Kanagawa University in 1971 and then a lecturer at The University of Tokyo in 1975. After serving as an associate professor (1978) and professor (1986), he became a professor at The University of Tokyo Graduate School of Engineering in 1995. He was appointed as the Chairman of the Kanagawa Academy of Science and Technology (KAST) and Director of the Functional Materials Research Laboratory of the Central Japan Railway Company in 2003. He was appointed as professor emeritus of The University of Tokyo and later became a special university professor emeritus of The University of Tokyo in 2005. He served as the chairman for the Chemical Society of Japan from 2006 to 2007 and has been the Director of the China Research Center at the Japanese Science and Technology Agency (JST) since 2008. He is a famous chemist with many prestigious awards and honors. Since 2010 he has been the president of Tokyo University of Science and the leader of Photocatalysis International Research Center (PIRC). He is known for significant contributions to the research of photocatalysis, photoelectrochemistry and diamond electrochemistry.

Shanhu Liu was born in 1977 in Henan Province, China. He received his PhD degree from Nanjing University (2010), and then joined in Henan University. Since 2011, he has been performing research as visiting scholar in Kanagawa Academy of Science and Technology, JSPS research fellow and Guest associate professor in Tokyo University of Science, successively, under the supervision of Prof. Akira Fujishima. His research interests focus on smart interfaces and photoelectrocatalysis.

1. Introduction

1.1. Synthetic diamond materials

Diamond materials, including the synthetic ones, are attracted attentions in various scientific and engineering fields due to their chemical stability and high hardness [1,2]. Owing to the outstanding electronic and electrochemical properties of diamond, progress has been made on applying diamond in fields like environmental protection, health care and biochemical applications [3–6]. Hydrogen-terminated diamond is an excellent kind of sensing material used in electrochemical and biological sensor devices. Most diamond systems involving photochemical and photo-electrochemical reactions do not require gem-quality diamonds, but rather millions of microscopic diamond crystals. The usage of diamond materials is an ideal solution to the problem rising from the degradation of interfaces of many traditional materials used in microelectronic devices (*e.g.* glass, silicon, and gold). Synthetic diamond materials, mainly as thin films and particles, have been especially attractive in the development of integrated sensors and devices because of good electrical, chemical, and biocompatible properties [7–9]. Photochemical and photo-electrochemical investigations on diamond would be helpful for deeply understanding of diamond-electrolyte systems, their photo activities, and diamond semiconductive properties.

Table 1
The band gap and work function of carbon materials (Ref. [23]).

	Bandgap (eV)	Work function (eV)
Amorphous carbon	0.2–3.0	4.9
Diamond	5.5	5.45
Graphite	0	5.0
Fullerene (C_{60})	1.6	4.6–5.0
Carbon nanotubes (CNT)	0.3–2.0	4.5–5.1
Graphene	0–0.3	5.0

The mainstream of synthetic diamond materials used in the photochemical and photo-electrochemical applications is semiconductive diamond films. Researchers now can prepare polycrystalline diamond through chemical vapor deposition (CVD) technology. To expand its application in photo-electrochemical field, preparation of Boron-doped diamond (BDD) thin films have been developed. As an ideal platform for optical, electrochemical, mechanic and electronic applications, BDD materials have excellent advantages including chemical robustness, wide electrochemical potential window, resistance to corrosion, low background current, optical transparency and biocompatibility [10,11], which make them the most popular diamond materials used in photochemical and photo-electrochemical applications. BDD thin layers can be deposited on quartz, glass, and polymer with optical transparency (about 300–1000 nm range) [13–15], which varies from ultrananocrystalline, through nanocrystalline, and polycrystalline to single crystal materials. When illuminated with light of certain wavelength and in an electrical field from outside, the photogenerated charge carriers in BDD films are accelerated and flow through the grain boundaries, generating an electron current that shows a diode-like behavior.

In addition, diamond nanoparticle (NDs, including diamond powder) and amorphous diamond (or diamond-like carbon, DLC) are sometimes employed in photo-involved applications. NDs are prepared by explosive method for the detonation of carbon materials. NDs materials with small size (normally 4–5 nm) have high specific surface areas, on which a large number of reactive chemical groups are located [16–19]. Amorphous diamond (or DLC), with tetrahedral carbon structures containing no non-carbon impurities and mixture with distorted sp^2 and sp^3 bonds, is also an excellent choice used in photo-electronic devices [20–22].

1.2. Diamond semiconducting property

The electrochemical and photo-electrochemical behavior of diamond materials have been studied in relation to their semiconducting characteristics. All the stable carbon allotropes, with a number of properties in photovoltaic industry, are listed in Table 1 [23,24]. They can work as insulators or semiconductors in the manner of diamond or diamond-like carbon, metallic and semi-metallic in the case of graphite or graphene, or conducting and semiconducting in the case of fullerene and carbon nanotubes [25].

Nowadays thin diamond films, which are widely used in laboratories and industry, can be prepared by CVD methods [9]. Until now tremendous progress has been made in the CVD technology for preparation of diamond materials on large-area silicon, Mo, quartz, glass, etc [9,13]. It was shown that synthetic polycrystalline diamond films by CVD devices, with different growth conditions, show a wide varieties of physical properties [26,27]. The differences include the layer thickness, grain size, surface roughness, and atom clusters. By doping of other elements, active impurities could be introduced into diamond showing p- or n-type conductivity, which is necessary for the applications in semiconductor devices [28]. By boron doping, p-type semiconducting (using holes as the

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