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Optical and structural properties of amorphous carbon thin films deposited by microwave surface-wave plasma CVD

Sudip Adhikari [a,*], Sunil Adhikary [b], Ashraf M.M. Omer [a], Mohamad Rusop [c], Hideo Uchida [b], Tetsuo Soga [c], Masayoshi Umeno [b]

[a] Department of Electrical and Electronic Engineering, Chubu University, 1200 Matsumoto-cho, Kasugai 487-850, Japan
[b] Department of Electronics and Information Engineering, Chubu University, 1200 Matsumoto-cho, Kasugai 487-8501, Japan
[c] Department of Environmental Technology and Urban planning, Nagoya Institute of Technology, Gokiso-cho, show-ku, Nagoya 466-8555, Japan

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Abstract

Nitrogen doped amorphous carbon (a-C:N) thin films were deposited on silicon and quartz substrates by microwave surface-wave plasma chemical vapor deposition technique at low temperature (<100 °C). We used argon (Ar), camphor dissolved in alcohol and nitrogen (N) as carrier, source and dopant gases, respectively. Optical band gap (E_g) decreased from 4.1 to 2.4 eV when the N gas concentration increased from 0 to 4.5%. The films were annealed at different temperatures ranging from 150 to 450 °C in Ar gas environment to investigate the optical and electrical properties of the films before and after annealing. Both E_g and electrical resistivity (ρ) decreased dramatically to 0.95 eV and 5.7×10^4 (Ω-cm) at 450 °C annealing. The structural modifications of the films leading to more graphite as a function of the annealing temperature was confirmed by the characterization of Raman spectra.

Keywords: Amorphous carbon; Nitrogen doping; Microwave surface-wave plasma CVD; Annealing; Optical band gap; Electrical resistivity

1. Introduction

Silicon (Si)-based solar cells fabricated to date are very expensive to use on a commercial basis [1,2]. The cost reduction of solar cells and establishment of environmentally friendly production process are very important for further spread of photovoltaic technology. Carbon is highly stable, cheap and non-toxic material which can be obtained from precursors those are sufficiently available in nature [3,4]. Furthermore, amorphous carbon (a-C) has been an attractive material for the fabrication of photovoltaic solar cells because of its outstanding properties such as chemical inertness, high hardness, high thermal conductivity, infrared optical transparency and optical band gap varying over a wide range from about 5.5 eV for insulating diamond to 0.0 eV for metallic graphite [5]. Unlike amorphous silicon (a-Si) where only the stable sp^3 configuration is possible, a-C consists of a mixture of sp^2 and sp^3 configurations and hence possible to vary the optical band gap (E_g) by simply varying the relative proportion of the sp^2/sp^3 hybridization [6]. Also, like other amorphous semiconducting materials, it can be doped and made n- or p-type [7]. The properties of a-C thin films depend strongly on the precursor material, method of deposition and thermal annealing. Hydrogen content in a-C thin films modifies the properties of the films by increasing the percentage of sp^3 configuration, causing an increase in the E_g [8]. Doping of a-C with n-type dopants such as phosphorus (P) and nitrogen (N) has been attempted by several researchers [5,9]. N being a gaseous phase has the advantage of better control of dopant concentration over P in physical deposition system. Successful control of N doping in a-C helps to realize the photovoltaic application. Although N doped a-C (a-C:N) films have been deposited by various methods [10,11], properties of a-C:N films deposited by microwave (MW) surface-wave plasma (SWP) chemical vapor deposition (CVD), an improved newly developed thin film deposition method [12] are not yet clearly understood.

In this paper, we report the optical, electrical and structural properties of a-C:N thin films deposited on silicon (Si) and

* Corresponding author. Tel.: +81 568 51 9244; fax: +81 568 51 1478.
E-mail address: te04801@isc.chubu.ac.jp (S. Adhikari).

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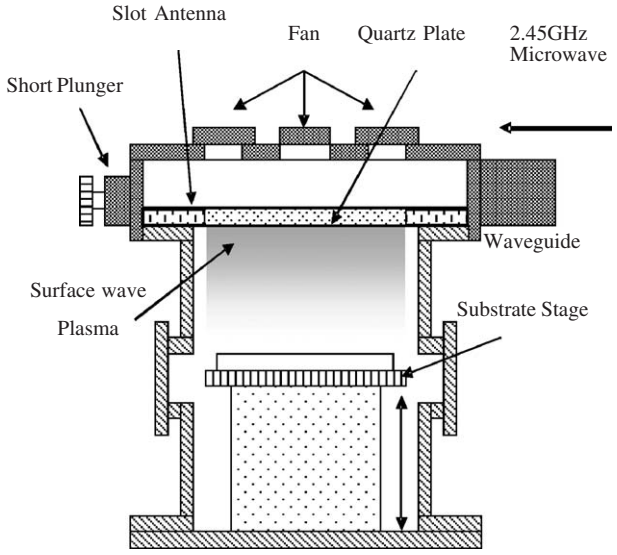

Fig. 1. Schematic diagram of MW SWP-CVD.

quartz substrates by MW SWP-CVD, before and after thermal annealing of the films. Our experimental purpose is to control properties of the films for suitable solar cell application.

2. Experimental setup

a-C:N thin films were deposited on Si and quartz substrates by MW SWP-CVD at low temperature (<100 °C). Fig. 1 shows schematic diagram of the MW SWP-CVD system. This method is useful to avoid plasma induced damages of the substrates surfaces and has a relatively large stage diameter (20 cm) that enables to deposit a relatively large area thin film in uniform condition. The SWP was produced in a 30 cm diameter cylindrical vacuum chamber by introducing 2.45 GHz microwave through a quartz window via slot antennae. The maximum MW power of the system is 2500 W, whereas stage temperature can be controlled up to 650 °C (±5 °C). In this deposition system MW power, gas flow rate and deposition duration can be controlled by touch-screen computer system. For film deposition, we used Ar (280 ml/min) as carrier gas, camphor ($C_{10}H_{16}O$) dissolved with ethyl alcohol (C_2H_5OH) (10 ml/min) composition as source gas and N (0 to 6.4% in the gas composition) as a doping gas.

The CVD chamber was evacuated at 3.5×10^{-4} Pa and total gas pressure was held fixed at 60 Pa during film deposition. The substrates were cleaned beforehand by acetone and methanol in ultrasonic bath and only for Si substrates were etched with diluted hydrofluoric acid ($HF:H_2O$) (1:10) in order to remove the native oxide layer from the surface. The lunched MW power was typically 500 W.

One set of the as-deposited a-C:N films was annealed in a quartz tube at different temperatures (150 to 450 °C) for 20 min in Ar gas environment. The as-deposited and the annealed-films were characterized by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), UV/VIS/NIR spectroscopy, Nanopics 2100/NPX200 surface profiler, 4-point probe resistance measurement and Raman spectroscopy.

3. Results and discussion

Fig. 2 shows AFM image of three-dimensional surface structure of the a-C:N film deposited on Si substrate as an example. The root mean square (RMS) roughness of the film was found to be 0.50 nm. The a-C:N thin films deposited by MW SWP-CVD are very smooth compared to a-C:N films deposited by other methods [13,14].

The analysis of XPS is one of the most useful techniques for characterization of the chemical bonding structure and to acquire useful information on the chemical environment. Fig. 3 shows the information of chemical composition in the as-

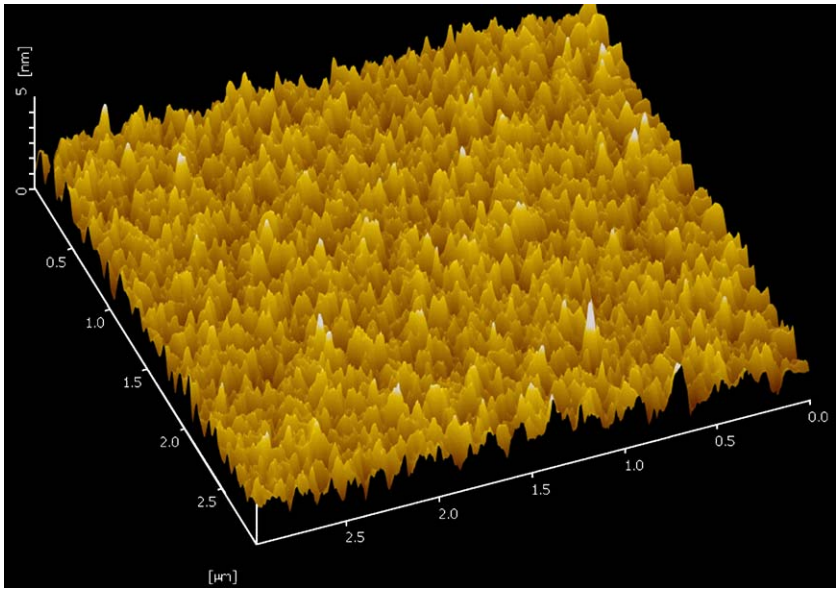

Fig. 2. AFM image (scanned area: 3×3 μm^2) of three-dimensional surface morphology of the a-C:N (N/Alcohol+Camphor flow ratio: 5:10) film deposited on silicon substrates. The RMS roughness of the film was found to be 0.50 nm.