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# Effects of methane gas flow rate on the optoelectrical properties of nitrogenated carbon thin films grown by surface wave microwave plasma chemical vapor deposition

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## Abstract

We have studied the influence of the methane gas ($CH_4$) flow rate on the composition, structural and electrical properties of nitrogenated amorphous carbon (a-C:N) films grown by surface wave microwave plasma chemical vapor deposition (SWMP-CVD) using Auger electron spectroscopy (AES), X-rays photoelectron spectroscopy (XPS), UV–visible spectroscopy, 4-point probe and 2-probe method resistance measurement. The photoelectrical properties of a-C:N films was also studied. We have succeed to grow a-C:N films using a novel method of SWMP-CVD at room temperature and found that the deposition rate, bonding, optical and electrical properties of a-C:N films are strongly dependent on the $CH_4$ gas sources and the a-C:N films grown at higher $CH_4$ gas flow rate have relatively high electrical conductivity for both cases of in dark and under illumination condition.


*Keywords:* Surface wave; Microwave; Methane; Gas flow rate; Amorphous carbon nitride; a-C:N

## 1. Introduction

There is a growing interest in amorphous carbon (a-C), hydrogenated amorphous carbon (a-C:H) and nitrogenated amorphous carbon (a-C:N) thin films because of their well-known outstanding properties such as carbon is a material of highly stable, cheap and non-toxic which can be obtained from precursors those are sufficiently available in nature, high hardness, high electrical resistivity, high thermal conductivity, high dielectric strength, infrared transparency and optical band gap varying over a wide range from that of insulating diamond (~5.5 eV) to that of metallic graphite (~0.0 eV) [1,2]. Recently, there have been many interests in the study of the properties of CVD grown a-C or diamond-like carbon (DLC) films as candidate materials for future new electronic devices.

The properties of amorphous carbon a-C films strongly depend on the precursor material and can be grown on silicon and quartz substrates at relatively low temperature using a varieties of deposition method such as pulsed laser deposition [3–6], ion beam deposition [7,8], sputtering [9,10], chemical vapor deposition (CVD) [11,12] and r.f./microwave plasma CVD [13–18]. The low temperature CVD is a great advantage from a few point of manufacturing aspect. Furthermore, the enlargement of a-C films required for a variety of industrial applications can be done using the large area plasma sources such as r.f. discharge plasmas.

Recently, a new deposition method, surface wave microwave plasma chemical vapor deposition (SWMP-CVD) has been developed [11,12]. This deposition technique is a new deposition method of carbon thin films without corroding ions on substrate. It is also noticed as one of promising plasma sources for the large area thin film deposition. To our knowledge, so far, methane or acetylene is commonly used as a precursor material in r.f./microwave plasma CVD deposition methods for the preparation of a-C thin films. Since structural, physical and optical properties of a-C thin films grown by SWMP-CVD are not yet understood, in this paper we report our latest result on the effect of methane gas on the properties of a-C:N films grown by SWMP-CVD.

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## 2. Experimental

We have employed the SWMP-CVD system for the deposition of a-C:N thin film at low temperatures. An image of experimental setup is shown in Fig. 1. The SWMP-CVD was produced in a 300 mm, cylindrical vacuum chamber by introducing a 2.45 GHz microwave through a quartz window via slot antenna. The microwave is introduced through the slot antennae drops exponentially below the quartz window where the electron density exceeds the cutoff density [12,13]. A high density plasma with a uniform electron density more than $10^{11}$ $cm^{-3}$ was formed in the vacuum chamber and broadened in the downed stream region due to the particle diffusion. Film deposition was carried out on the quartz, glass and p-type (100) silicon (Si) wafer substrates with a resistivity of 5–10 Ω-cm and a thickness of 600 μm. Before deposition, the substrates were cleaned before-hand by acetone and methanol for each at approximately 5 min in an ultrasonic bath and only for Si substrates were etched with HF:$H_2O$ (1 : 10) in order to remove the resistive native oxide formed over the surface. After cleaning, the substrates were quickly transferred into the chamber, placed on the substrate holder and then exposed in the chamber with Argon plasma discharges for approximately 30 min.

The deposition chamber was then evacuated to a base pressure approximately at $2 \times 10^{-4}$ Pa using a turbo molecular pump for approximately 4 h. The launched microwave power was set approximately at 500 W and the total pressure was set approximately at 50 Pa, where the gas flow rates were 280 ml/min for Argon gas and 5 ml/min for nitrogen gas ($N_2$). The methane gas flow rate was the variable condition from 5 to 20 ml/min. The films were deposited at room temperature. The reference sample of a-C thin film, thereafter also referred to as Sample A, has also been prepared on quartz and n-type Si substrate using the above procedure with fixed methane gas flow rate at 5 ml/min and deposition without in $N_2$ gas ambient. All the thin films were analyzed by using standard experimental characterization techniques [8].

Table 1
The deposition rates, surface roughness and nitrogen contents of the a-C:N films as a function of $CH_4$ gas flow rates

| Methane ($CH_4$) gas flow rates (ml/min) | Deposition rate (nm/min) | Surface roughness (nm) | Nitrogen content (at.%) |
|---|---|---|---|
| Sample A | 7.6 | 1.9 | 0 |
| 5 | 6.1 | 1.4 | 6.3 |
| 10 | 8.4 | 2.1 | 6.9 |
| 15 | 9.3 | 2.5 | 7.5 |
| 20 | 10.5 | 2.8 | 8.1 |

## 3. Results and discussions

The maximum average deposition rate (DR) of SWMP-CVD film was calculated as the quotient of the measured average thickness and the deposition time. Should be noted here that, when calculating the deposition rate from the thickness, the changes in the density and roughness of the film have not been taken into account, therefore, the deposition rates might become more and more over estimated as film density decreases and roughness increases with higher $CH_4$ gas partial pressures. The deposition rate and surface roughness as a function of $CH_4$ gas partial pressures is shown in Table 1.

We discovered that, for the a-C:N films grown at 5 ml/min, the DR was decreased and the surface morphology was smoother compared with Sample A, which deposited in the same range of the corresponding parameter without $N_2$ gas

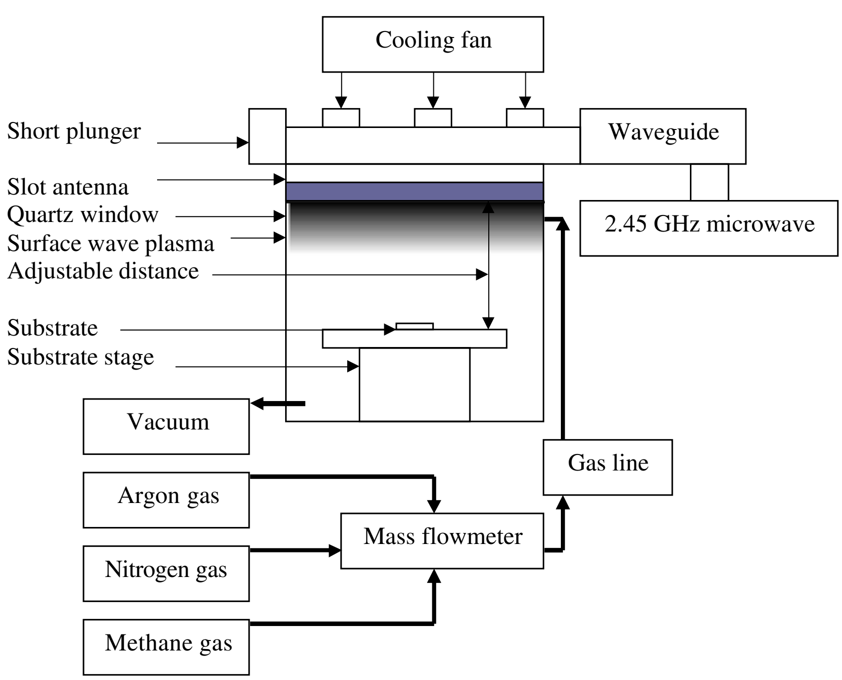


Fig. 1. The image of surface wave microwave chemical vapor deposition (SWMP-CVD) systems.