

**DEPOSITION OF A-SiC:H FILMS ON AN UNHEATED SI SUBSTRATE BY
LOW FREQUENCY (50Hz) PLASMA Cvd****M. Shimosuma, K. Ibaragi*, M. Yoshion**, H. Date, K. Yoshida and H. Tagashira***College of Medical Technology, Hokkaido University, Sapporo 060, Japan***Department of Electrical Engineering, Hokkaido University, Sapporo 060, Japan****Hokkaido Polytechnic College, Zenibako 3-190, Otaru 047-02, Japan**Kitami Institute of Technology, Kitami 090, Japan**Hokkaido Institute of Technology, Sapporo 006, Japan***ABSTRACT**

Hydrogenated amorphous silicon carbide (a-SiC:H) films have been deposited on unheated substrates by low frequency (50Hz) plasma using SiH₄+CH₄+H₂ gas mixtures. Deposition rate, refractive index, optical band gap, Vickers hardness and IR spectrum of the deposited a-SiC:H films have been measured for various ratios of gas flow rates $k(=CH_4/SiH_4, 0.5k4)$ with a constant H₂ flow rate (100sccm). As k increases, the deposition rate of the a-SiC:H films increases up to the maximum value of about 220nm/h at k=2.5, and then it decreases. The refractive index of the films was 2.6 for k=2.5, while the optical band gap of the films was 3.3eV for k=2.2. The maximum value of Vickers hardness of the films was 1500Hv at k=1. The infrared transmission measurement shows that the films contain both Si-C and Si-CH₃ bonds.

INTRODUCTION

Hydrogenated amorphous silicon carbide (a-SiC:H) is a wide-band-gap, high breakdown field, high thermal conductivity, high melting point, high surface hardness and high transparency material. Because of its properties, a-SiC:H films are used in semiconductor devices, such as solar cells and high power electronic switches [1]. Therefore, it is necessary to investigate the techniques to deposit a-SiC:H film. In general, a-SiC:H films are deposited on a heated (300~400) substrate by thermal and high frequency (rf) plasma CVD (Chemical Vapor Deposition).

In this work, a-SiC:H films have been fabricated by deposition on an unheated sub-

strate by a low frequency (50Hz) plasma CVD method [2-4] using SiH₄+CH₄+H₂ gas mixtures. Deposition rate, refractive index, optical band gap, Vickers hardness and IR spectrum of the deposited a-SiC:H films have been measured for various ratios of gas flow rates $k(=CH_4/SiH_4, 0.5k4)$, with a constant H₂ and SiH₄ flow rates. As k increases, the deposition rate of the a-SiC:H films increases up to the maximum value of about 220nm/h at k=2.5, and then it decreases. The refractive index of the films decreases with increasing k, and is 2.6 for k=2.5 while the optical band gap of the films increases with increasing k, and is 3.3eV for k=2.2. The Vickers hardness of the films decreases slightly from the maximum value of 1500Hv

at $k=1$. The infrared transmission measurement shows that the films contain both Si-C and Si-CH₃ bonds. Moreover, the light emission spectrum from excited plasma in SiH₄+CH₄+H₂ mixture by 50Hz power was measured. The emission from excited states of Si, CH, H and H₂ was observed. These results suggest that the a-SiC:H films deposited by the present 50Hz plasma (without substrate heating) possess the high quality required for semiconductor device materials.

EXPERIMENTAL

The experimental apparatus is similar to that of reference 3 and shown schematically in Fig. 1. Briefly, the plasma reactor was evacuated by a diffusion pump backed by a rotary pump. The steel plasma reactor is 40 cm in diameter and 60 cm in height. The electrodes were made of 15 cm diameter stainless steel plate with 2 cm gap between the two electrodes. The 50 Hz power is supplied at the upper electrode, and the lower is grounded. The 50 Hz plasma was excited between the

two electrodes, and silicon plate substrates were placed on the substrate holder on the lower electrode.

No substrate heater was equipped in this system, and all the results were obtained at room temperature (about 20). The gases used in the experiment were SiH₄ (99.95%), CH₄ (99.995) and H₂ (99.99999%). These gases were introduced in the reactor at a rate of 5 sccm, 2.

520 sccm and 100 sccm, respectively. Conditions for deposition of a-SiC:H film in this work are listed in Table. The deposition rate, refractive index, optical band gap, Vickers hardness and IR spectral transmittance of the deposited SiC films were measured as a function of $k(=CH_4/SiH_4, 0.5k_4)$. The emission spectrum from the SiH₄+CH₄+H₂ gas mixture plasma was measured by a monochromator with a photomultiplier. The photomultiplier has adequate sensitivity in the range of 200 to 800 nm.

Table 1. Conditions for deposition of a-SiC:H film

plasma current	5mA
gap length	2cm
gas pressure	1Torr
power frequency	50Hz
substrate temperature	room temperature(unheated)
substrate material	Si
gas flow SiH ₄	5.0sccm
CH ₄	2.5~20.0sccm
H ₂	100sccm

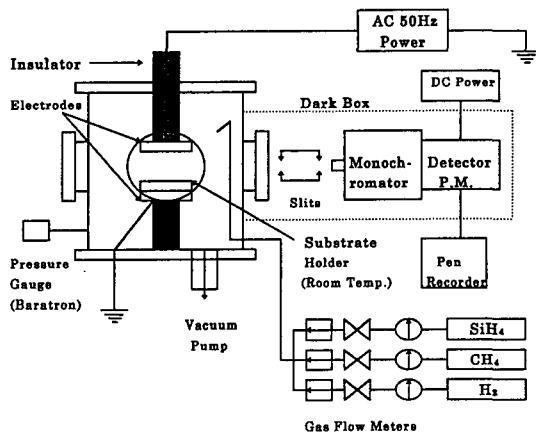


Fig. 1 Schematic diagram of experimental setup.

RESULTS AND DISCUSSIONS

Emission spectrum of a-SiC:H film deposition plasma:

The light emission spectrum from excited

plasma in $\text{SiH}_4 + \text{CH}_4 + \text{H}_2$ (5, 10 and 100sccm, respectively) mixture by 50Hz power was measured. The emission from excited states of Si, CH, H and H_2 was observed from the mixture plasma in a wave length range from 200 to 600 nm. The emission from excited atomic carbon was not observed. Fi. 2 shows a typical emission spectrum from SiH_4 , CH_4 and H_2 mixture plasma. The emission lines from excited Si atoms (255 nm and 288 nm), excited H atoms (H: 656 nm and H:486 nm), excited CH molecules (431 nm and 389 nm) and excited H_2 molecules were the major lines. From these results, the atomic and molecular radical species by the 50 Hz plasma were those dissociated from SiH_4 , CH_4 and H_2 , having many high energy electrons⁵. Therefore, it seems that 50Hz plasma CVD is a suitable method for a-SiC:H film deposition without substrate heating.

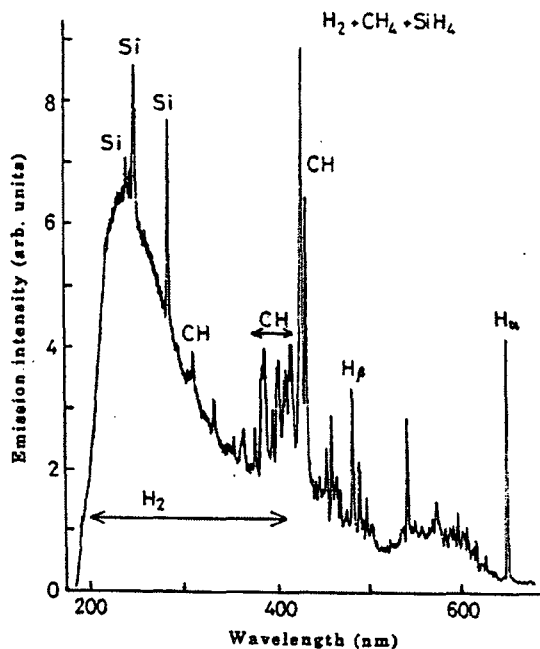


Fig. 2 Emission intensity from $\text{H}_2 + \text{CH}_4 + \text{SiH}_4$ mixture 50Hz plasma at $k(\text{CH}_4/\text{SiH}_4) = 2$

Properties of deposited a-SiC:H film:

The deposition rate of a-SiC:H films with 50Hz plasma CVD at room temperature is shown in Fig. 3 as a function of the ratio of gas flow rates $k = \text{CH}_4/\text{SiH}_4$, with constant SiH_4 and H_2 flow rates (5 and 100sccm, respectively).

The deposition rate of a-SiC:H film increases with increasing k until it reaches the maximum value of about 220 nm/h at $k = 2.5$, and then it decreases. The dependence is similar to a plasma CVD result using three gases mixture by other workers⁶.

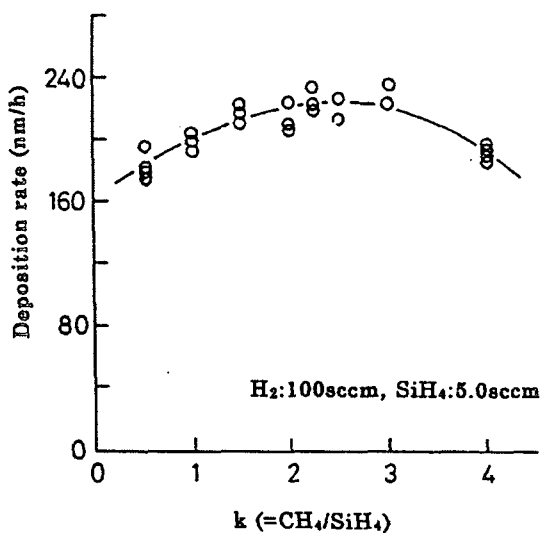


Fig. 3 Deposition rate as a function of k .

Fig. 4 shows the refractive index of deposited a-SiC:H film as a function of k . The refractive index of the films was measured by ell-psometry. The refractive index of the deposited a-SiC:H film decreases with increasing k . The refractive index of the deposited films at $k = 0.5$ and 4 were 3.5 and 2.4, and these values were respectively those of the refractive index of a-Si:H and a-C:H. The refractive index of stoichiometric SiC is

known to be 2.65. In order to obtain the refractive index of 2.6, the value of k was about 2.5.

Fig. 5 shows the infrared transmission result of the deposited a-SiC:H film on unheated Si substrate by 50Hz plasma CVD at $k=1$. As indicated in Fig. 5, the a-SiC:H film contains both Si-C (bending mode) and Si-CH₃ (stretching mode) bonds, which is typical of plasma CVD 7. From the infrared experiment, increase of the infrared absorption of Si-CH₃ (980cm⁻¹) with increasing k was observed.

Fig. 6 shows the optical band gap of deposited a-SiC:H film on unheated substrate by 50 Hz plasma CVD as a function of k . The optical band gap increases with increasing k , and is 3.3eV at $k=2.2$. The optical band gap of 3.3eV is a value of the stoichiometric SiC. In Fig. 6, it seems that it tends to the value of a-C:H with increasing k , because the optical band gap of a-C:H by 50Hz plasma CVD was about 4.0eV⁴. On the other hand, the optical band gap at $k > 1$ decreased and tend

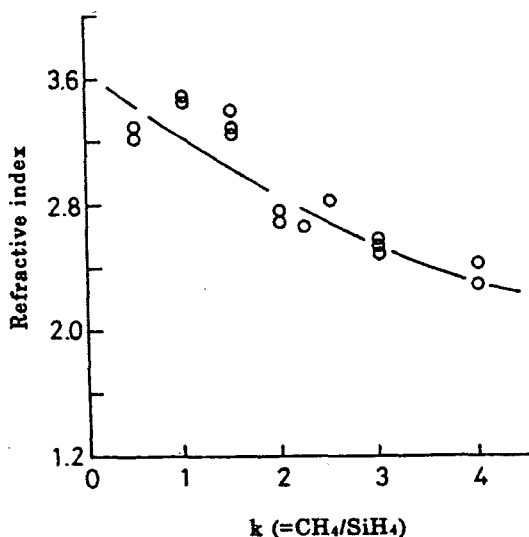


Fig. 4 Refractive index as a function of k .

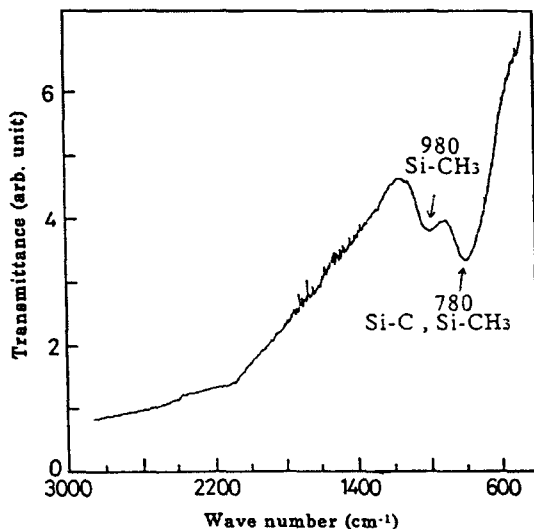


Fig. 5 Infrared spectral transmittance at $k=1$.

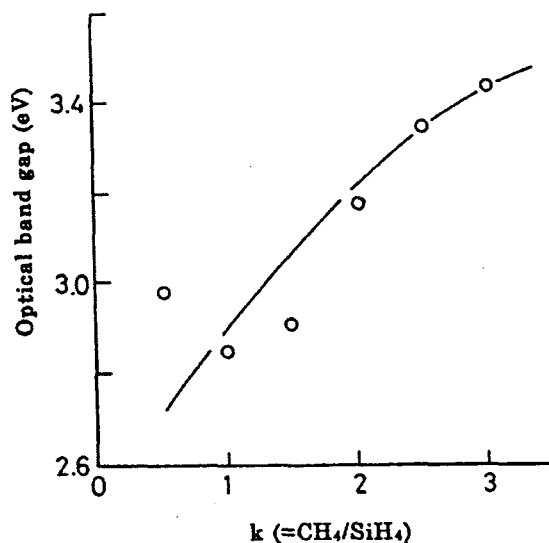


Fig. 6 Optical band gap as a function of k .

to the optical band gap of a-Si:H. The deposited a-SiC:H film was highly transparent and showed very uniform interference color. The surface morphology of the deposited film was observed by SEM, and it had mirror like uniformity.

Vickers hardness of deposited a-SiC:H film on unheated Si substrate by 50Hz plasma CVD is shown in Fig. 7 as a function of k . As k increases, the Vickers hardness of the a-SiC:H film increases up to the maximum value of about 1500Hv at $k=1$, and then it decreases.

From these results, it was suggested that high quality a-SiC:H film deposition on unheated substrate was performed by 50Hz plasma CVD using $\text{SiH}_4 + \text{CH}_4 + \text{H}_2$ mixtures in a range of $1 < k = (\text{CH}_4/\text{SiH}_4) < 2$.

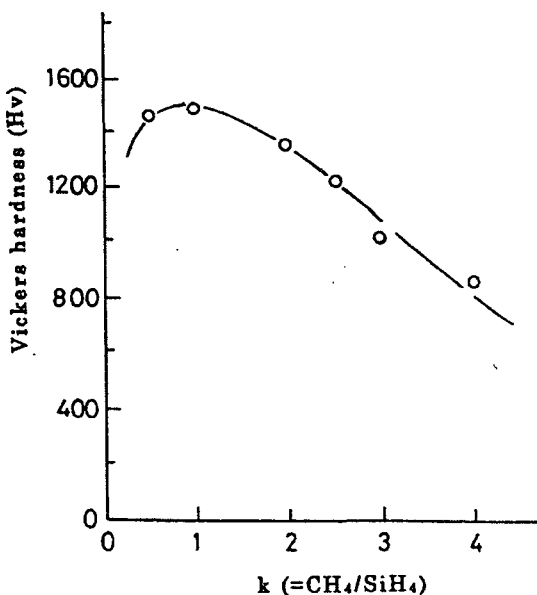


Fig. 7 Vickers hardness as a function of k .

CONCLUSION

a-SiC:H films have been fabricated by deposition on unheated Si substrate using a low frequency (50Hz) plasma of $\text{SiH}_4 + \text{CH}_4 + \text{H}_2$ gas mixtures. Deposition rate, refractive index, optical band gap, Vickers hardness and IR spectrum of the deposited a-SiC:H films have been measured for various ratios of

gas flow rates $k (= \text{CH}_4/\text{SiH}_4, 0.5k_4)$, with a constant H_2 flow rate.

The light emission spectrum from excited plasma in $\text{SiH}_4 + \text{CH}_4 + \text{H}_2$ mixture by 50Hz power was measured. The emission from excited states of Si, C, H and H_2 was observed from the mixture plasma. The atomic and molecular radical species by the 50Hz plasma were those dissociated from SiH_4 , CH_4 and H_2 . As k increases, the deposition rate of the a-SiC:H films increases up to the maximum value of about 220 nm/h at $k=2.2$, and then it decreases. The refractive index of the films decreases with increasing k , and is 2.6 for $k=2.5$, while the optical band gap of the films increases with increasing k , and is 3.3eV for $k=2.2$. The deposited a-SiC:H film was highly transparent and showed very uniform interference color. As k increases, the Vickers hardness of the a-SiC:H film increases up to the maximum value of about 1500Hv at $k=1$, and then it decreases. The infrared transmission measurement shows that the films contain both Si-C and Si-CH₃ bonds.

These results suggest that the a-SiC:H films deposited without substrate heating by the present 50Hz plasma possess the high quality required for semiconductor device materials.

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