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Si Grain-Free Highly Conductive Microcrystalline SiC Films Prepared by Using Organic Silane Gas

K.Sasaki, T.Miyajima*, H.Hosoya** and S.Furukawa

Interdisciplinary Graduate School of Science and Engineering
Tokyo Institute of Technology
4259 Nagatsuda, Midori-ku, Yokohama 227, Japan

ABSTRACT

Aiming at producing Si heterojunction materials, a preparation method of μc-SiC film by means of ECR plasma CVD using organic silane gas ($Si(CH_3)_2H_2$) is described. Si-C bond in the gas molecule is effective for nucleating SiC crystalline. The μc-SiC film does not contain Si grain. N is found to act as a dopant impurity. The film resistivity is as low as $10^4 \Omega$cm in spite of having large C composition (C/Si=0.5) and wide optical bandgap of 2.6~2.8eV.

1. INTRODUCTION

We have shown the fundamental feasibility of wide emitter type Si-HBT's using available wide bandgap materials such as μc-Si and a-SiC[1]. Simultaneously, through the device research in the amorphous emitter HBT system, we have indicated problems to be solved[2]. In order to realize advanced integrated circuits using the Si-HBT's, development of more suitable wide bandgap materials for the heteroemitter are desired.

SiC based materials, referred as μc-SiC or SiC_x, are considered to be promising for heteroemitter materials[3),4)]. However, in general, they contain small crystalline Si grains or consist of mixture of a-SiC and μc-Si[5),6)]. On the view point of reducing the emitter resistance, which significantly degrades high speed device performance, heteroemitter region should be made as thin as possible within the extent of not losing the wide bandgap effects. In the case of using these films for the emitter under very thin condition, if the film thickness is being close to the Si grain size, homogeneity of the film can not be satisfied because of the film structure. Concretely speaking, wide bandgap emitter is short-circuited by the Si grains, resulting that wide bandgap features would disappear. Hence, for the heteroemitter material of Si-HBT, SiC films containing no Si grain is necessary.

Present Affiliation
* Nippondenso R&D Dept.
**Mazda

We have successfully developed Si grain-free μc-SiC film using organic silane gas ($Si(CH_3)_2H_2$) by low temperature process by means of ECR plasma CVD technique. In this paper we will show the preparation method of the μc-SiC films and discuss growth mechanism, energy bandgap and doping characteristics by introducing N impurity.

2. EXPERIMENTS

Film preparation was carried out by using ECR (Electron Cycrotron Resonance) plasma CVD apparatus (AFTEX-4000UX) consisting of 3 chambers, that is, plasma excitation chamber, film preparation chamber and load locked chamber. H_2 gas was introduced into the first chamber, where the ECR plasma was generated by supplying 2.45GHz microwave and 875Gauss magnetic filed. The plasma condition was sensitive to magnetic field and during the plasma was maintained, little reflection of microwave power was observed.

Two types of source gases, SiH_4-CH_4 and $Si(CH_3)_2H_2$, were introduced into the second chamber and were examined to prepare SiC films. Also, PH_3 and NH_3 gases were used for the n-type impurity doping source.

The films were deposited on chemically cleaned Si wafer and quartz substrates which were placed on a temperature controlled heater block. The gas pressure was typically order of 10^{-3}Torr.

3. RESULTS AND DISCUSSION

3-1 Film Preparation by SiH_4-CH_4 Gas System

For the film preparation using SiH_4-CH_4 source gas, as the results were summarized in Fig.1, a desired μc-SiC film has not been obtained, although preparation conditions were widely changed. The reasons are speculated as follows: H_2 plasma has an effect of bringing about nucleation of Si crystallite while H radicals reject loosely bonded C atoms from the SiC growing surface. As a result, supplying too much H_2 plasma, poly- or μc-Si film has been prepared. Also, when C atoms are introduced in the film, randomly supplied C species induce amorphousization, resulting in amorphous film structure.

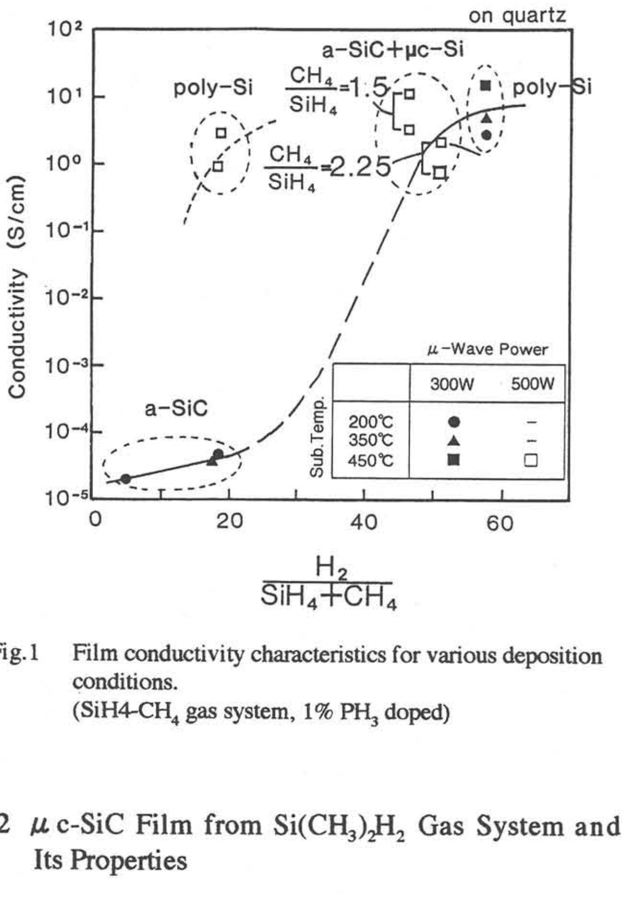

Fig.1 Film conductivity characteristics for various deposition conditions.
($SiH4$-CH_4 gas system, 1% PH_3 doped)

3-2 μc-SiC Film from $Si(CH_3)_2H_2$ Gas System and Its Properties

X-ray diffraction patterns for the films prepared by using $Si(CH_3)_2H_2$ source gas are shown in Fig.2. (Here, the same amount of CH_4 gases as $Si(CH_3)_2H_2$ was added). Broad but clear peaks are observed around $2\theta = 35°$ which is assigned as 3C-SiC(111). Considering that the similar peaks are observed in spite of widely changing the substrate temperature, unintentional heating effect by plasma or microwave would be neglected. For SiH_4-CH_4 gas system, a strong Si(220) diffraction peak is observed while remarkably, for this gas system, there is no peak for Si crystallite in the spectra. Moreover, C/Si

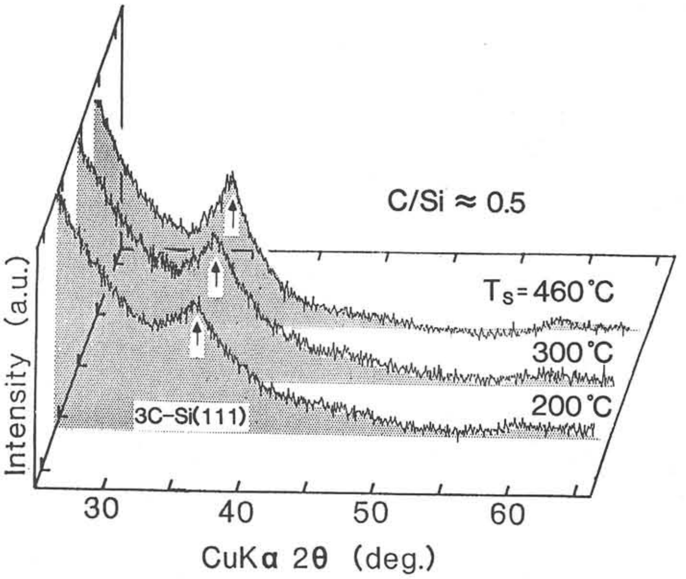

Fig.2 Substrate temperature dependence of X-ray diffraction patterns.
($Si(CH_3)_2H_2$ gas system, μ-wave power = 900W)

composition ratio is near even in spite that C/Si ratio in gas phase is 3.

In order to investigate the differences of decomposition property between the two gas systems, optical emission property was measured. The spectra are shown in Fig.3. The strong emission peaks from Si and SiHn (marked by*) are observed for SiH_4-CH_4 gas system while interestingly they are very weak for $Si(CH_3)_2H_2$ gas system. From these facts, it is considered that for $Si(CH_3)_2H_2$ gas system, Si-C bonds in the source gas are preserved and transported to the substrate surface. If Si-C bonds were broken in the plasma, a similar result as SiH_4-CH_4 gas system would be led.

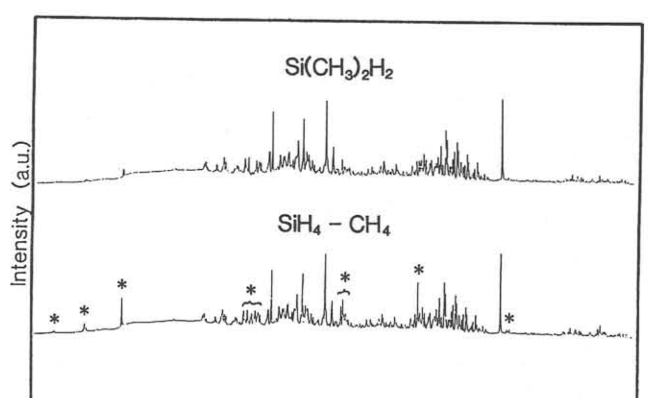

Fig.3 Optical emission spectra of ECR plasma for SiH_4-CH_4 and $Si(CH_3)_2H_2$ gas system. Emission peaks relating to Si and SiHn are marked by *.

The mechanism of the SiC crystalline formation would be speculated as follows: Si-C bonds in the $Si(CH_3)_2H_2$ gas molecules have an effect of nucleation of SiC crystalline by giving regularity of atom stacking rule to the film structure. In addition, polarity of the gas molecule may enhance it.

Impurity doping properties were investigated by using NH_3 and PH_3 gases as doping source. The preliminary results are shown in Fig.4. Here, dopant ratio in gas phase is adopted as x-axis. The electrical resistivity ρ is not so low as μc-Si or μc-SiC reported[3),6)]. The reasons of the resistivity may be due that the μc-SiC in this work does not contain Si grain, in addition, a-SiC portion surrounding crystalline SiC grain has large C composition hence large resistivity. Nevertheless, comparing this μc-SiC with conventional a-SiC, the resistivity is lowered. Interestingly, N is found to become a dopant in this μc-SiC film as same as in c-SiC and the resistivity decreases to as low as 10^4 Ωcm order by NH_3 doping.

Photo-absorption property was measured and the optical energy bandgap $E_{g(opt)}$ was estimated by extrapolation of $(\alpha h\nu)^{1/2}$-$h\nu$ plot. The results were plotted as a function of doping ratio in Fig.4. In lightly doped region, wide bandgap of 2.6~2.8eV is obtained. As increasing P doping, energy bandgap decreases. This may be due to increase of localized states near energy band edge. On the contrary, for N doping, energy bandgap increases. This reason is probably due to formation of nitride without increase of localized states.

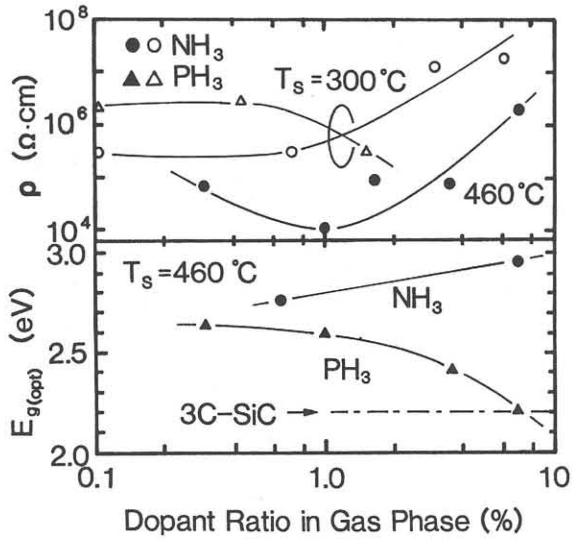

Fig.4 Electrical resistivity and optical energy bandgap of μc-SiC films as a function of dopant ratio in gas phase.

4. CONCLUSION

Organic silane gas is found to be effective for formation of SiC crystalline phase in the low temperature ECR plasma CVD process. In addition, the μc-SiC film prepared by this method do not contain Si crystalline grain. Therefore, this film can be used for a heterojunction under extremely thin condition. Furthermore, it was made clear that for this μc-SiC film, N acts as a dopant as same as c-SiC. Also, it can be said that this film has low resistivity considering near even C/Si composition and wide energy bandgap of 2.6 ~2.8eV.

This film is considered to be useful for not only a heteroemitter material of Si-HBT but also solar cell and light emitting device applications.

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