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Heptafluoroisopropyl Methyl Ether as a Low Global Warming Potential Alternative for Plasma Etching of SiC

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Abstract

Heptafluoroisopropyl methyl ether (HFE-347mmy) was used for SiC etching to evaluate low-GWP (global warming potential) hydrofluoroether as an alternative to SF₆. SiC was etched in the HFE-347mmy/O₂/Ar and SF₆/O₂/Ar plasmas, and the etching characteristics were compared at various bias voltages. The etch rates of SiC in the HFE-347mmy/O₂/Ar plasma were higher than those in the SF₆/O₂/Ar plasma at low bias voltages (lower than – 500 V), whereas those in the SF₆/O₂/Ar plasma were higher than those in the HFE-347mmy/O₂/Ar plasma at high bias voltages (higher than – 600 V). The relative amounts of F and O radicals in both plasmas imply that F is a major contributor to SiC etching at low bias voltages (lower than – 500 V), whereas O is a major contributor at high bias voltages (higher than – 600 V) in the HFE-347mmy/O₂/Ar and SF₆/O₂/Ar plasmas. AFM measurements showed that the SiC etched in the HFE-347mmy/O₂/Ar plasma exhibited smoother surfaces than that etched in the SF₆/O₂/Ar plasma.

Keywords Plasma etching · SiC · Global warming potential · HFE-347mmy · Bias voltage

Introduction

Current Si-based power semiconductors face limitations in high-temperature and high-voltage applications owing to their narrow energy band gap (1.1 eV) and low dielectric strength (0.3 MV/cm), leading to power loss. As an alternative to Si, silicon carbide (SiC) has drawn attention because it can be operated under severe environments, such as high temperatures and currents, owing to its wide energy band gap (3.2 eV) and high dielectric strength (3 MV/cm) [1–3].

SiC etching is usually conducted in plasmas containing fluorinated gases such as CHF₃, CF₄, NF₃, and SF₆ mixed with O₂ [4–8], because SiC is etched such that F reacts with Si or C to form volatile SiF₄ or CF₄ and O reacts with C to form volatile CO and CO₂ [4]. However, these fluorinated gases cause environmental concerns owing to their high global warming potentials (GWPs) (CHF₃—14,600, CF₄—7300, NF₃—17,400, and SF₆—25,200). These gases are also mainly used for the etching of dielectrics such as SiO_2 and Si_3N_4 [9–12], and several classes of alternative compounds have been evaluated to replace high-GWP fluorinated gases with lower-GWP etchants, including unsaturated fluorocarbons [13, 14], hydrofluoroethers [15–17], and hydrofluoroalcohols [18]. However, there are few reports on the use of low-GWP etchants for SiC etching.

In this study, plasma etching of SiC using heptafluoroisopropyl methyl ether (HFE-347mmy) and SF₆ was investigated to compare their etching characteristics. HFE-347mmy belongs to hydrofluoroether with a GWP of 392, significantly lower than that of SF₆. The etching characteristics of SiC etching were studied by varying the bias voltage applied to the substrate.

Experimental

SiC etching was performed in an inductively coupled plasma (ICP) system, as previously described [17]. Two 13.56-MHz radio-frequency powers were independently applied to ignite the plasma (source power) and bias the sample (bias power).

The HFE-347mmy/O₂/Ar and SF₆/O₂/Ar plasmas were used for SiC etching. The pressure in the ICP chamber was maintained at 30 mTorr. The source power was fixed at 250 W, whereas the bias voltage (equivalent to the bias

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power) was varied from -400 to -700 V. The flow rates of HFE-347mmy and SF₆ were both 3 sccm. The flow rates of O₂ and Ar were 7 and 5 sccm, respectively, in both the HFE-347mmy/O₂/Ar and SF₆/O₂/Ar plasmas; therefore, the total flow rates of both plasmas were 15 sccm, respectively.

The sample was an n-type 4H–SiC substrate, and each sample was rectangular ($10 \times 5 \text{ mm}^2$). The etch rates of SiC were obtained by measuring the changes in the thickness of the SiC substrate using a surface profiler (Ambios Technology, XP-1) after the etching process. The relative amounts of F and O radicals produced in the plasma were determined using optical emission spectroscopy (OES; Avantes, AvaSpec-ULS2048-USB2-RM). Atomic force microscopy (AFM; PSIA, XE-150) with a scan area of $5 \times 5 \mu m^2$ was used to observe the roughness of the etched surfaces.

Results and Discussion

Figure 1 shows the etch rates of SiC in the HFE-347mmy/ O₂/Ar and SF₆/O₂/Ar plasmas as a function of bias voltage. The etch rates of SiC increased monotonically with the bias voltage in both the HFE-347mmy/O₂/Ar and SF₆/O₂/Ar plasmas. However, the degree to which the etch rate changed differed between the HFE-347mmy/O₂/Ar and SF₆/O₂/Ar plasmas. At a bias voltage of – 400 V, the etch rate of SiC in the HFE-347mmy/O₂/Ar plasma was 10.6% higher than that in the SF₆/O₂/Ar plasma. The difference in the etch rates decreased with increasing bias voltage, and the etch rates reversed near – 600 V. Finally, at a bias voltage of – 700 V, the etch rate in the SF₆/O₂/Ar plasma was 3.4% higher than that in the HFE-347mmy/O₂/Ar plasma.

To understand the differences in the etch rates at various bias voltages in the HFE-347mmy/ O_2 /Ar and SF₆/ O_2 /



Fig. 1 Etch rates of SiC in HFE-347mmy/O2/Ar and SF6/O2/Ar plasmas as a function of bias voltage

Ar plasmas, the relative amounts of F and O radicals were investigated using OES because F and O are the main etchants for SiC etching. SiC is etched such that F reacts with Si or C to form volatile SiF_4 or CF_4 and O reacts with C to form volatile CO and CO_2 .

Figure 2 shows the intensities of the optical emission peaks of the F and O radicals produced in the HFE-347mmy/ O_2/Ar and $SF_6/O_2/Ar$ plasmas, respectively, as a function of bias voltage. The intensities of the F and O peaks increased monotonically with the bias voltage in both the HFE-347mmy/O₂/Ar and SF₆/O₂/Ar plasmas. However, the relative magnitudes of the optical emission intensities of each radical (F and O) depended on the type of plasma. In other words, the F-peak intensities in the HFE-347mmy/O₂/ Ar plasma were higher than those in the $SF_6/O_2/Ar$ plasma, whereas the O-peak intensities in the $SF_6/O_2/Ar$ plasma were higher than those in the HFE-347mmy/O2/Ar plasma at all bias voltages. Since both F and O are responsible for SiC etching, the more F or O is present, the more SiC is etched. The OES results imply that SiC etching is mainly affected by F if the etch rate of SiC is higher in the HFE-347mmy/O₂/Ar plasma than that in the $SF_6/O_2/Ar$ plasma, whereas etching is mainly affected by O if the etch rate is higher in the $SF_6/$ O₂/Ar plasma than that in the HFE-347mmy/O₂/Ar plasma.

As shown in Fig. 1, the etch rates of SiC in the HFE-347mmy/O₂/Ar plasma were higher than those in the SF₆/ O₂/Ar plasma at low bias voltages (lower than – 500 V), whereas the etch rates in the SF₆/O₂/Ar plasma were higher than those in the HFE-347mmy/O₂/Ar plasma at high bias voltages (higher than – 600 V). Combining the etch rate behavior with the relative amounts of F and O in the HFE-347mmy/O₂/Ar and SF₆/O₂/Ar plasmas, it can be said that



Fig. 2 Intensity of the optical emission peaks of F and O radicals produced in HFE-347mmy/O₂/Ar and $SF_6/O_2/Ar$ plasmas, respectively, as a function of bias voltage



Fig. 3 RMS roughness of the SiC surface etched in HFE-347mmy/ O_2/Ar and $SF_6/O_2/Ar$ plasmas at various bias voltages

F is a major contributor to SiC etching at low bias voltages (lower than -500 V), whereas O is a major contributor at high bias voltages (higher than -600 V) in the HFE-347 mmy/O₂/Ar and SF₆/O₂/Ar plasmas. This may be due to the differences in the bond energies of Si-C (4.3 eV) and C-C (6.3 eV). As mentioned earlier, SiC etching is performed by the reaction of F with Si or C to form volatile SiF_4 or CF_4 and the reaction of O with C to form volatile CO and CO₂. At low bias voltages, the C-C bond was not sufficiently broken compared with the Si-C bond, leading to a greater contribution of F to SiC etching than that of O. This resulted in a higher etch rate of SiC in the HFE-347mmy/O₂/ Ar plasma owing to the higher number of F radicals in the HFE-347mmy/O₂/Ar plasma in the low bias voltage regime. However, at high bias voltages, O began to play an important role in SiC etching because of the sufficient dissociation of the C-C bond. Since more O radicals were present in the $SF_6/O_2/Ar$ plasma, the etch rates of SiC were higher in the $SF_6/O_2/Ar$ plasma than in the HFE-347mmy/O₂/Ar plasma in the high bias voltage regime.

During the plasma etching of SiC, the surface of SiC is subject to be damaged by ion bombardment, affecting several aspects such as subsequent processes and device performance. To compare the degree of surface damage in the HFE-347mmy/O₂/Ar and SF₆/O₂/Ar plasmas, the roughnesses of the etched surfaces were measured using AFM. Figure 3 shows the root mean square (RMS) roughness of the SiC surface etched in the HFE-347 mmy/O₂/Ar and SF₆/O₂/Ar plasmas at various bias voltages. Although the magnitude of the RMS roughness was small and the RMS roughness variation with the bias voltage was also small, the RMS roughness was lower in the HFE-347mmy/O₂/ Ar plasma than in the SF₆/O₂/Ar plasma, indicating that SiC etching in the HFE-347mmy/O₂/Ar plasma provided smoother surfaces.

Conclusions

SiC etching in HFE-347mmy/O2/Ar plasma was investigated at various bias voltages and compared with etching in $SF_6/$ O₂/Ar plasma. The etch rates of SiC in the HFE-347mmy/ O_2/Ar plasma were higher than those in the SF₆/O₂/Ar plasma at low bias voltages (lower than - 500 V), whereas those in the $SF_6/O_2/Ar$ plasma were higher than those in the HFE-347mmy/O₂/Ar plasma at high bias voltages (higher than - 600 V). OES measurements revealed that the F-peak intensities in the HFE-347mmy/O2/Ar plasma were greater than those in the $SF_6/O_2/Ar$ plasma, whereas the O-peak intensities in the $SF_6/O_2/Ar$ plasma were greater than those in the HFE-347mmy/O2/Ar plasma at all bias voltages. This implies that F is a major contributor to SiC etching at low bias voltages (lower than -500 V), whereas O is a major contributor at high bias voltages (higher than -600 V) in the HFE-347mmy/O₂/Ar and SF₆/O₂/Ar plasmas. The insufficient dissociation of the C-C bonds in SiC at low bias voltages was responsible for the reduced reaction of O with C to form volatile products, making F a major contributor to SiC etching at low bias voltages.

SiC etching using the HFE-347mmy plasma provided higher etch rates than the SF₆ plasma at specific bias voltages. In addition, AFM measurements showed that SiC etching using HFE-347mmy plasmas provided smoother surfaces than SF₆ plasmas. Therefore, this study reveals the feasibility of using HFE-347mmy, whose GWP is significantly lower than that of SF₆, in SiC etching as an alternative to SF₆.

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