

J.J.Wang,⁽¹⁾ E.S.Lambers,⁽¹⁾ S.J.Pearton,⁽¹⁾ M.Ostling,⁽²⁾ C.-M.Zetterling,⁽²⁾ J.M.Grow,⁽³⁾
 F.Ren,⁽⁴⁾ R.J.Shul,⁽⁵⁾

(1) Dept. Materials Science and Engineering, University of Florida, Gainesville FL 32611

(2) Royal Institute of Technology, Kista, Sweden

(3) New Jersey Institute of Technology, Newark, NJ 07102

(4) Bell Laboratories, Lucent Technologies, Murray Hill, NJ 07974

(5) Sandia National Laboratories, Albuquerque, NM 87185

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ABSTRACT

A number of different plasma chemistries, including NF_3/O_2 , SF_6/O_2 , SF_6/Ar , ICl , IBr , Cl_2/Ar , BCl_3/Ar and $\text{CH}_4/\text{H}_2/\text{Ar}$, have been investigated for dry etching of 6H and 3C-SiC in a Inductively Coupled Plasma tool. Rates above $2,000 \text{ \AA}\cdot\text{cm}^{-1}$ are found with fluorine-based chemistries at high ion currents. Surprisingly, Cl_2 -based etching does not provide high rates, even though the potential etch products (SiCl_4 and CCl_4) are volatile. Photoresist masks have poor selectivity over SiC in F_2 -based plasmas under normal conditions, and ITO or Ni are preferred.

INTRODUCTION

There has been a revival of interest in SiC-based high power, high temperature ($>250^\circ\text{C}$) devices and circuits for applications ranging from advanced avionics, automobiles, and space exploration to bore-hole logging.⁽¹⁻²⁰⁾ SiC is the most mature of the candidate semiconductors, which include diamond and GaN, and has the advantage of high thermal conductivity and availability in both bulk, single-crystal and thin-film form. The two most common polytypes are 6H and 4H, although cubic material (3C) is also available^(3,7,10,20). There are a wide variety of device structures that have been fabricated in 6H, including thyristors, static induction transistors, Schottky diodes, metal-semiconductor field effect transistors (MESFETS) and various vertical Metal-Oxide-Semiconductor (MOS) devices.⁽¹⁻²⁰⁾

In all of these structures there is a need for pattern transfer capability. While some success has been obtained with photo-chemical etching in electrolytes that oxidize the SiC surface and subsequently dissolve this oxide^(21,22), it is generally agreed that conventional wet chemical etching is not possible at practical temperatures. This places a strong emphasis on development of high quality dry etch processes. Most of the plasma etching to date has been performed with capacitively-coupled reactors, particularly reactive ion etching (RIE), with fluorine-based gas chemistries.⁽²³⁻²⁹⁾ One attribute of this technique is the high ion energy (typically $\geq 200 \text{ eV}$), which is useful in breaking the bonds in the SiC. However a downside to high ion energies is mask erosion and residual lattice damage in the semiconductor. The etch products with fluorinated plasma chemistries are SiF_x and CF_x species, and under high bias conditions (i.e. physically-dominated process) these probably do not need to be fully fluorinated (i.e. $x = 4$) to be desorbed from the surface by ion assistance. Alternative plasma chemistries include Cl_2 -, Br_2 - or I_2 -based gases, but these produce slower etch rates than the F_2 -based mixtures. Rather than rely simply on high ion energy to stimulate etching of the SiC, another approach is to employ a high ion flux with lower ion energy.⁽³⁰⁻³⁷⁾ This is the basis of the newer high density plasma tools in vogue for pattern transfer in Si. Etching of SiC in Electron Cyclotron Resonance (ECR)^(30,36) and

Inductively Coupled Plasma (ICP)⁽³⁷⁾ reactors has been reported by several groups, with fairly good etch rates and good anisotropy. The operating pressure (1-2mTorr) of these tools is much lower than in RIE systems (10-300 mTorr), with much higher ion fluxes ($\geq 10^{11} \text{ cm}^{-3}$ compared to $\geq 10^9 \text{ cm}^{-3}$). A major advantage with the newer reactors is the ability to separately control ion flux and ion energy, leading to increased flexibility in designing etch products.

In this paper we report a parametric investigation of the etching characteristics of 6H-SiC bulk wafers and thin film SiCN in ICP NF_3 -based plasma chemistries. The etch yields have been measured as a function of both ICP source power (which controls ion flux) and rf chuck power (which controls ion energy) and the effect of gas additive (Ar or O_2) on etch rate determined. The removal rate of both SiC and SiCN and etch anisotropy is found to be a function of atomic fluorine neutral density, ion flux and ion energy. The resulting surface roughness is almost independent of plasma composition for SiC, but for SiCN surface morphology degrades at high NF_3 percentages in the gas feedstock. The surfaces are chemically clean over a wide range of conditions, with only small concentrations of either N- or F- containing residues detected.

EXPERIMENTAL

The SiC samples were bulk substrates doped with either Al ($p = 6 \times 10^{18} \text{ cm}^{-3}$) or N ($n \sim 5 \times 10^{18} \text{ cm}^{-3}$), and both with (100) orientation. The $\text{SiC}_{0.5}\text{N}_{0.5}$ layers were grown on Si substrates using chemical vapor deposition with a tris-dimethylamino silane precursor, and were $\sim 5,000 \text{ \AA}$ thick and nominally undoped. Some of the samples were patterned with AZ5209E photoresist or $\sim 3,000 \text{ \AA}$ thick indium tin oxide (ITO) masks. Flemish et.al.^(30,32,36) have previously shown that ITO provides much better etch resistance during high density plasma processing of SiC with F_2 -based mixtures than photoresist. All of the experiments were performed in a Plasma Therm 790 system. The samples are located on a He backside cooled chuck biased with 13.56MHz of power. The plasma is generated in a 2MHz, 1500W, 4- turn plasma coil geometry source and the pressure was held constant at 2mTorr. Electronic grade NF_3 , O_2 and Ar gases were fed into the ICP source through mass flow controllers at total flow rates of 15 standard cubic centimeters per minute (sccm). Experimental process parameters were plasma composition, rf chuck power and ICP source power. Etch rates were obtained from stylus profilometry measurements of the samples after mask removal. Scanning Electron Microscopy (SEM) was used to examine etch anisotropy and surface morphology, while Atomic Force Microscopy (AFM) was employed to quantify the surface roughness. Optical Emission Spectroscopy (OES) was used to monitor plasma species.

RESULTS AND DISCUSSION

A common feature of fluorine-based plasmas under capacitively coupled conditions is that addition of O_2 at ratios by flow of 10-35% can increase the atomic fluorine neutral concentration⁽³⁸⁾. We examined the optical emission spectra of both NF_3/O_2 and NF_3/Ar discharges, as shown in Figure 1. Surprisingly there was little significant difference in atomic fluorine concentration (confirmed by actinometric analysis using the 7451 nm Ar line), which suggests the ICP source is already very efficient in dissociating the NF_3 . The spectra in Figure 1 also show little evidence of molecular continua, confirming the high dissociation efficiency.

These results are reflected in the etch rate data of Figure 2, which show SiC and SiCN removal rates as a function of NF_3 percentage in NF_3/O_2 and NF_3/Ar for fixed source power, pressure and

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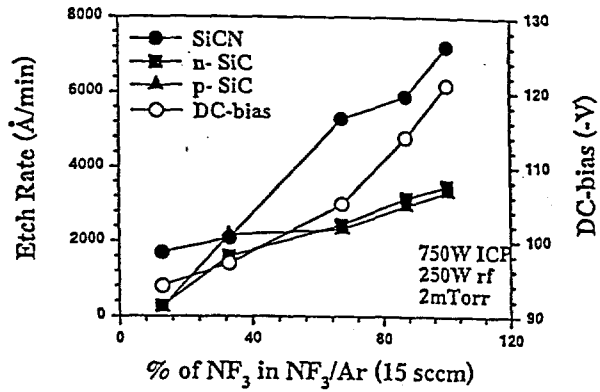
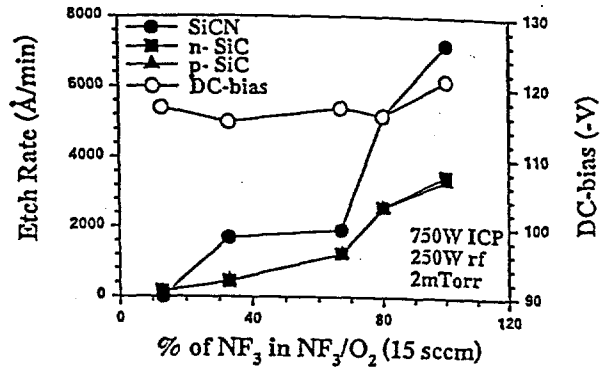
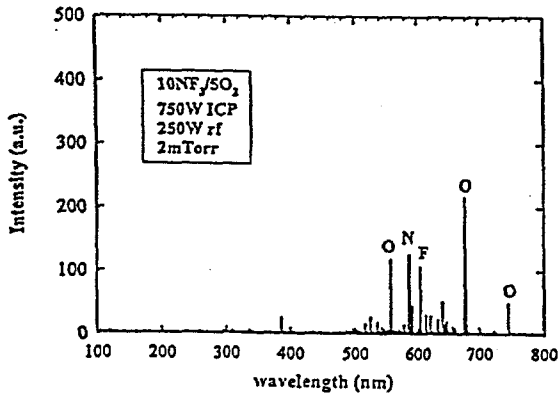
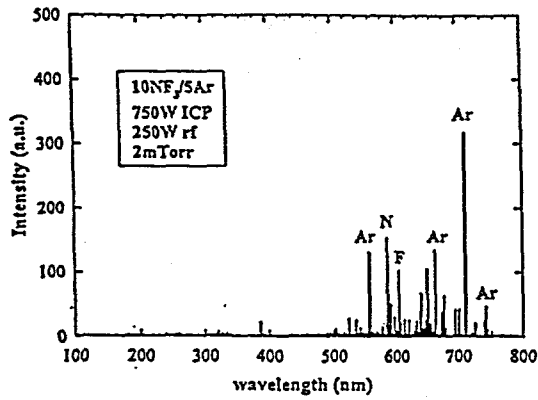


Figure 1. Optical emission spectra of ICP discharges (750W source power, 2mTorr, 250W rf power) of either 10NF₃/5Ar (top) or 10NF₃/5O₂ (bottom).

Figure 2. Etch rates of p⁺ SiC, n⁺ SiC and SiCN in 750W source power, 2mTorr, 250W rf chuck power discharges as a function of NF₃ percentage in either NF₃/O₂ (top) or NF₃/Ar (bottom).

rf chuck power. There are several interesting aspects of the data. First, the rates are slightly higher with NF₃/Ar, which suggests that ion bombardment plays a role in the etch mechanism. Since the etch products (SiF_x and CF_x, where x ≤ 4) are quite volatile, it is likely that more efficient bond-breaking in the SiC rather than ion-enhanced desorption of these products, is the reason for this trend. Second, there is no measurable difference in etch rates between n⁺ and p⁺ SiC, indicating that Fermi level effects play no role in the etch mechanism. Third, the etch rates increase monotonically with NF₃ percentage in both chemistries, which indicates that the limiting step is supply of atomic fluorine to the surface under these conditions. Fourth, the rates for SiCN are significantly higher than for SiC in both plasma chemistries, probably due to the high vapor pressure of the NF_x etch products and to the probable lower crystalline quality of the thin film SiCN relative to the bulk SiC, which is grown at much higher temperatures. Fifth, there is a finite etch rate for both materials in NF₃/Ar even at the lowest NF₃ percentage, whereas there is a threshold concentration for the commencement of etching in NF₃/O₂ discharges. Sixth, the behavior of dc self-bias with plasma composition is quite different in the two plasma chemistries. While it stays relatively constant in NF₃/O₂ suggesting that ion density also remains approximately constant, there is a monotonic increase with NF₃ percentage in NF₃/Ar. In the latter case this indicates that the conductivity of the plasma is decreasing as NF₃ increases, leading to a higher self-bias. The associated higher ion energy is also a contributing factor to the higher etch rates with NF₃/Ar relative to NF₃/O₂.

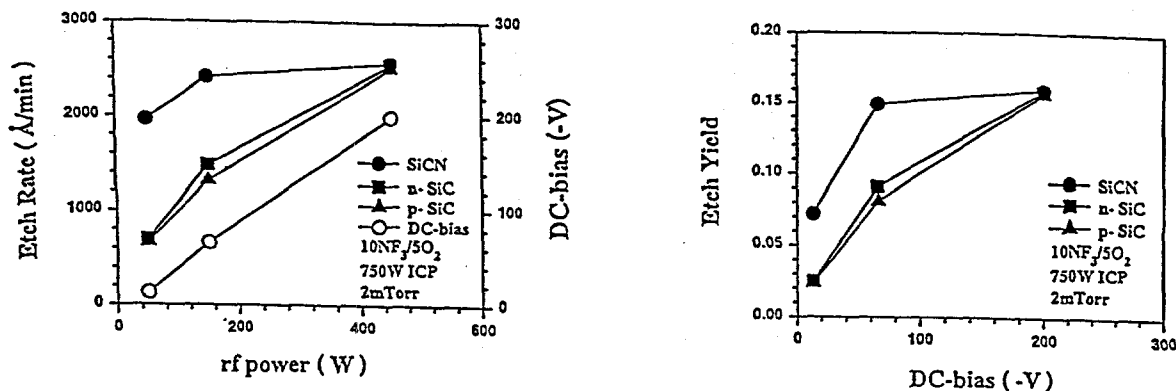


Figure 3. Etch rates of SiC and SiCN as a function of rf chuck power in 10NF₃/5O₂, 2mTorr, 750W source power discharges (left) and etch yield of the same materials as a function of dc chuck self-bias (right).

Figure 3 shows etch rates as a function of rf chuck power (left) and etch yield as a function of dc self-bias (right). For SiC there is a monotonic increase in etch rate with bias, which again emphasizes the strong role of ion energy in the etch mechanism. The average ion energy is the sum of the dc self-bias voltage and plasma potential (roughly ~20V in this tool). For SiCN the etch rate saturates as this bias is increased and this may be related to sputter-induced removal of the atomic fluorine before it can react with the surface. Note that the etch yields indicate are relatively low, but the resulting etch rate is high because of the high ion flux.

As the source power is increased at constant rf chuck power, the dc self-bias is strongly suppressed and the competing factors of increasing ion flux and decreasing ion energy produce the resulting maximum in etch rate at ~1000W source power. Note that the etch rate for SiC can still be above 1,000 Å/min even at very low bias values provided the ion flux is high.

The features were quite anisotropic and the etched surface was smooth. There was some slight degree of trenching at the base of the sidewalls, which was also reported by Flemish et al.^(30,33,36) for ECR CF₄-based etching of SiC and is usually ascribed to glancing angle collisions of ions with the sidewall that produce enhanced etching at the foot of the sidewall. The combination of high ion flux and high ion energy produced substantial faceting of the ITO mask. This led to sloped sidewalls and trenching at the foot of the picture. By contrast, if ion energy was reduced under these conditions by lowering of chuck power to 250W, the chemical component of the etching is enhanced and leads to significant sidewall undercut. It is clearly necessary to balance the physical and chemical contributions in order to optimize the anisotropy of the etched features.

The surface roughness of both SiCN and SiC was examined after etching by AFM. The plasma composition dependence of root-mean-square (RMS) roughness is plotted in Figure 4 for SiCN, n⁺ SiC and p⁺ SiC. The values for SiCN go through a minimum at ~33% NF₃ by flow in NF₃/O₂, and become very high as the NF₃ percentage is increased. We did not perform Auger Electron Spectroscopy (AES) in these samples, but we suspect that the surface becomes non-stoichiometric through preferential loss of one of the lattice constituents (probably N because NF₃ is the most volatile of the prospective etch products). The SiC samples showed stoichiometric surfaces over the whole range of plasma compositions, with very small quantities (≤0.2at%) of N- or F- containing residues in some cases. This indicates that Si and C are being removed at equal rates under a wide range of conditions and that the etch products, once formed, are readily leaving the surface.

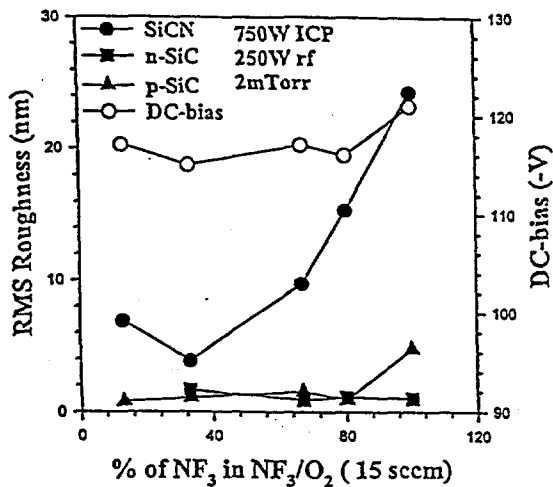


Figure 4. RMS roughness of SiC, n^+ and p^+ SiC measured by AFM after etching in NF_3/O_2 discharges (750W source power, 250W rf chuck power, 2mTorr) as a function of plasma composition.

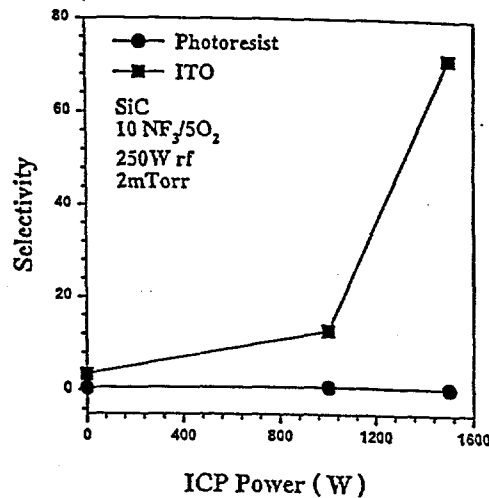


Figure 5. Etch selectivity for SiC relative to ITO and photoresist as a function of ICP source power in $10NF_3/5O_2$, 250W chuck power, 2mTorr discharges.

A final issue of practical interest in the etch selectivity of the SiC with respect to the two mask materials, photoresist and ITO. Figure 5 shows this data as a function of source power in $10NF_3/5O_2$, 2mTorr, 250W rf chuck power discharges. As expected there is no selectivity with respect to photoresist, but the ITO has excellent etch resistance⁽³⁶⁾, which increases as source power is increased due to the associated reduction in ion energy. A basic problem with dry etching of SiC is that the F-based chemistries which are most effective have poor selectivity for SiO_2 , SiN_x and resist, requiring the use of non-standard mask materials.

SUMMARY AND CONCLUSIONS

ICP NF_3 -based discharges produce smooth pattern transfer in SiC and SiCN at high rates (~3,500 Å/min in both n^+ and p^+ SiC, and ~7,500 Å/min in SiCN thin films.) The surface morphology of SiC was essentially independent of plasma composition in NF_3/O_2 discharges, but SiCN was much more sensitive to the atomic fluorine concentration. The etch rates of both SiC and SiCN were strong functions of ion flux, ion energy and fluorine concentration. This is consistent with the idea that the initial bond-breaking in the materials is an important step in the etch mechanism and this is enhanced at high ion fluxes and ion energies. Provided that there are sufficient weakened or broken bonds available for atomic fluorine to bond to, then the concentration of this reactant becomes the limiting step. The advantage of using NF_3 is that it is more readily dissociated than CF_4 or SF_6 and the combination with an ICP source means that ion energy, ion flux and atomic neutral density can be readily adjusted to produce high fidelity pattern transfer.

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