

Threshold Ion Energies and Cleaning of Etch Residues During Inductively Coupled Etching of NiO/Ga₂O₃ in BCl₃

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ABSTRACT

BCl₃ is an attractive plasma etchant for oxides because it is a Lewis acid used to scavenge native oxides on many semiconductors due to the strong B-O bonding. We investigated BCl₃-based dry etching of the NiO/Ga₂O₃ heterojunction system. BCl₃/Ar Inductively Coupled Plasmas produced maximum etch rates for NiO up to 300 Å.min⁻¹ and 800 Å.min⁻¹ for β-Ga₂O₃ under moderate plasma power conditions suitable for low damage pattern transfer. The selectivity for NiO: Ga₂O₃ was < 1 under all conditions. The ion energy threshold for initiation of etching of NiO was between 35-60 eV, depending on the condition and the etch mechanism was ion-driven, as determined by the linear dependence of etch rate on the square root of ion energy incident on the surface. By sharp contrast, the etching of Ga₂O₃ had a stronger chemical component, without a well-defined ion energy threshold. The as-etched NiO and Ga₂O₃ surfaces show chlorine residues, which can be removed on both materials by the standard 1NH₄OH: 10H₂O or 1HCl: 10H₂O rinses used for native oxide removal. According to the location of the Cl 2p_{3/2} peak, the Cl is ionically bonded.

Introduction

One of the major drawbacks of β -Ga₂O₃ is the lack of p-type dopants with shallow ionization energies ⁽¹⁻⁵⁾. This means that at room temperature, the maximum hole concentration is impractically low, although, native p-type conductivity can be observed at high temperatures due to native Ga vacancies (V_{Ga}), which are acceptors ^(4,7-9). An alternative approach is to use p-type oxides such as Cu₂O ⁽¹⁰⁾ or NiO ⁽¹¹⁻¹³⁾ to form heterojunctions with n-type Ga₂O₃. In particular, the NiO provides a relatively wide process window, where the electrical properties can be tuned by the deposition parameters ^(14,15). Both power rectifiers ^(12,13,16-27) and UV photodetectors ⁽¹¹⁾ have been demonstrated in this system. Common to any device structure is the need to pattern the NiO and possibly the Ga₂O₃. There are some initial studies of dry etching of Ga₂O₃ but little on heterojunctions with NiO or on the etch residues remaining on the surface ⁽²⁸⁻³²⁾. Etch rates of NiO were reported to be only 100 nm.min⁻¹ in Inductively Coupled Plasmas (ICP) using Cl₂/Ar or BCl₃/Ar chemistries ⁽³³⁾. Instead of the Cl₂ plasma chemistry typically used for Ga₂O₃ ⁽³⁴⁻³⁶⁾, substitution with BCl₃ gas should have advantages because the B–O bonding of 8.39 eV is much stronger than the Cl–O bonding of 2.82 eV. The latter is too weak to form a reactive layer with oxygen in metal oxides ⁽³⁷⁾. This means that BCl₃ is widely employed to remove native oxides on semiconductors and prevent incubation delays where the prevalent chlorine plasma cannot break through the native oxide ⁽³⁸⁾.

In this paper we report the threshold ion energies for dry etching of NiO in BCl₃ discharges, the selectivity to β -Ga₂O₃, and the cleaning of chlorine-based residues remaining on the surface after plasma exposure. There was a threshold ion energy of ~35-60 eV for NiO dry etching, whereas Ga₂O₃ did not have discernable ion energy for initiation of etching, suggesting a stronger chemical etching component. Finally, standard surface cleaning steps

were found to be effective in removing chlorine residues from the etched surfaces of both NiO and Ga₂O₃.

Experimental

The 190 nm thick NiO layers were deposited by magnetron sputtering on glass slides in a Kurt Lesker system at 3mTorr working pressure and 150W of 13.56 MHz power using two targets to achieve a deposition rate around 2 Å.sec⁻¹. The O₂/Ar gas ratio was 1/10, producing polycrystalline films with bandgap 3.75 eV, resistivity 0.1Ω.cm, and density 5.6 g.cm⁻³. The β-Ga₂O₃ samples used were (100) bulk, Sn-doped substrates, grown by the Edge-Fed Defined Growth method and purchased from Novel Crystal Technology (Saitama, Japan). All the samples were patterned with PR1045 photoresist and etched in a PlasmaTherm 790 reactor. Discharges with 15 sccm of BCl₃ and 5 sccm of Argon at a fixed pressure of 5mTorr were used to etch the NiO and Ga₂O₃. Etch rates were obtained by measuring the etch depth with a Tencor profilometer after the removal of the photoresist.

The near-surface composition of the NiO and Ga₂O₃ after dry etching was examined with X-Ray Photoelectron Spectroscopy (XPS), using a Physical Instruments ULVAC PHI, with an Al x-ray source (energy 1486.6 eV, source power 300W), analysis size of 100 μm diameter, a take-off angle of 50° and acceptance angle of ±7 degrees. The electron pass energy was 23.5 eV for high-resolution scans. The atomic percentages were calculated using CasaXPS software. To remove the chlorinated residues from the surface, we examined two standard cleaning mixtures, namely, 1NH₄OH: 10H₂O or 1HCl: 10H₂O for 60 secs. Both of these rinses are used for native oxide removal.

Results and Discussion

Figure 1 shows the NiO and Ga₂O₃ etch rates in the BCl₃/Ar ICP discharges as a

function of ICP source power at fixed rf chuck power of 150W. The chuck power controls the energies of the positive ions incident on the powered electrode where the samples sit, while the ICP power controls the ion density in the discharge. These ions will include Ar^+ , as well as positively charged fragments of the BCl_3 molecules. As ICP power is increased the ion energy is decreased due to the increase in ion density. This is also shown in Figure 1. The dc bias decreases from about 380 V at 200W ICP power to $\sim 270\text{V}$ at 600W ICP power. The ion energy is the sum of this self-bias, plus the plasma sheath potential, which is about 25V in this system. Thus, the average ion energies decrease from about 405eV to $\sim 295\text{ eV}$ as ICP power increases from 200 to 600 W. The etch rates of both materials increase monotonically with ICP power, showing that the increased ion density more than compensates for the decrease in ion energy. The increase of the NiO and Ga_2O_3 etch rates with ICP source power is due to the increase of the positive ion density. The etch rate of NiO is smaller than that of Ga_2O_3 for all ICP powers investigated, which is consistent with a lower degree of chemical etch component.

Figure 2 (a) and (b) show the etch rates of the two materials as a function of rf power at different ICP powers. The corresponding dc self-biases are shown in Figure 2 (c), showing the direct correlation of bias with rf power, with the overall magnitude reduced as ICP power is increased. The increases in etch rates with bias indicate a component of ion-driven mechanism in both cases, but the dependence is stronger for the NiO, which is consistent with the lower volatilities of the NiCl_x -based etch products.

The selectivity for etching one material over another is simply the ratio of their etch rates under the same conditions. Figure 3 (a) shows the NiO/ Ga_2O_3 selectivity as a function of rf power at the lowest ICP power we used, 150W. The selectivity is essentially constant

over the range of rf powers investigated. However, at higher rf powers, the selectivity increases, as shown in Figure 3 (c). This shows that the ion energy is the dominant factor determining the selectivity above a certain threshold ion energy, while the selectivities are almost independent of plasma density. The selectivity for etching NiO is always <1 , which is not desirable for selective patterning of NiO films on Ga₂O₃. The two approaches for overcoming this would be to use low etch rate conditions and carefully restrict the over-etch time during the plasma exposure time, or to include a thin etch stop layer between the NiO and the Ga₂O₃ which could then be selectively removed by a wet etch step.

We have reported previously that for etch processes where the ion-assisted etching mechanism is important, the etch rate (ER) is given by ⁽³⁹⁻⁴¹⁾

$$ER = J_+ A_{sat} (\sqrt{E} - \sqrt{E_{th}})$$

where J_+ is the positive ion flux, A_{sat} is a proportionality constant dependent on the specific plasma-material combination, E is the ion energy, and E_{th} is the threshold energy for initiation of etching. Figure 4 (a) shows there is a linear relationship between the etch rate of both NiO and Ga₂O₃ versus the square root of ion energy. This suggests the etching for both materials is ion-flux limited ⁽³⁹⁻⁴¹⁾. The intercept in plots like Figure 4 (a) is the approximate threshold ion energy ⁽³⁷⁾. This analysis worked for the NiO, with E_{th} being ~ 35 -60 eV for BCl₃/Ar in our system. These are fairly similar to the reported threshold ion energies for etching NiO in Cl₂/Ar ⁽³²⁾.

However, this approach did not work for Ga₂O₃ samples in Figure 4 (a), where the plot has a negative intercept on the x-axis, which indicates there is also a significant chemical etching component. Similarly, under conditions of low rf power, corresponding to low ion energy, neither material showed a realistic threshold within the analysis above, since

the slopes are negative in Figure 4 (b). These are conditions where chemical etching plays a more significant role.

Survey XPS spectra from the two types of materials after etching and subsequent cleaning in either 1NH₄OH: 10H₂O or 1HCl: 10H₂O rinse are shown in Figure 5(a) for NiO and Figure 5(b) for Ga₂O₃. It is noticeable that there are small Cl-related residues on the surfaces of both materials after the BCl₃ etching. An expanded view of the Cl 2p peaks for each sample is shown in Figure 6 (a) for NiO and Figure 6 (b) for Ga₂O₃. The Cl bonds are likely to be metal bonds rather than covalent bonds according to the location of the Cl 2p peak ^(43,44). Table I summarizes the near-surface atomic compositions of the samples before and after the cleaning rinses. The NiO has 15.7 % Cl in this near-surface region, much higher than the 3.7% on the Ga₂O₃ surface. This is consistent with the lower etch rates and lower volatilities of the NiCl_x etch products. Note that both cleaning procedures are effective in completely removing the chlorine-related surface residues. These are both standard processes for removing native oxides on compound semiconductor surfaces, so they fit well into any device processing sequence that includes a dry etching step.

Summary and Conclusions

The use of NiO with n-type Ga₂O₃ has shown promising device results, but the details such as the choice of plasma chemistry for dry etching, the threshold ion energies for etching, and the subsequent surface cleaning processes have been lacking. The use of the BCl₃/Ar plasma chemistry is attractive because of the scavenging effect of this Lewis acid on native oxides. We found this chemistry has selectivity <1 for NiO over Ga₂O₃, with an ion-flux-limited regime operative for NiO over a wide range of conditions. For NiO, the etch rate is independent of the reactive neutral flux in the ion-flux-limited regime. Standard

surface cleaning rinses were found to be effective in removing chlorinated residues. There is more scope for modification of surface properties using plasma processes, as there have been recent reports the valence and conduction band offsets of the $\text{NiO}_x/\beta\text{-Ga}_2\text{O}_3$ heterojunction decrease with F plasma pre-treatment ⁽⁴⁵⁾.

Acknowledgments

The work at UF was performed as part of Interaction of Ionizing Radiation with Matter University Research Alliance (IIRM-URA), sponsored by the Department of the Defense, Defense Threat Reduction Agency under award HDTRA1-20-2-0002. The content of the information does not necessarily reflect the position or the policy of the federal government, and no official endorsement should be inferred. The work at UF was also supported by NSF DMR 1856662 (James Edgar).

Data Availability

The data that supports the findings of this study are available within the article and its supplementary material.

Declarations

The authors have no conflicts to disclose.

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Table 1. Near-surface compositions of NiO and Ga₂O₃ samples after exposure to BCl₃/Ar plasmas and then subsequent cleaning in NH₄OH or HCl rinse.

Samples	Atomic percentage (%)			
	O 1s	C 1s	Ni 2p	Cl 2p
NiO as-etched	55.42	11.07	17.81	15.70
HCl clean	62.05	8.65	29.3	0
NH ₄ OH clean	69.87	8.4	21.51	0.22

Samples	Atomic percentage (%)			
	O 1s	C 1s	Ga 2p ₃	Cl 2p
Ga ₂ O ₃ as-etched	68.88	10.27	17.21	3.73
HCl clean	35.07	0	64.93	0
NH ₄ OH clean	39.27	0	60.73	0

Figure Captions

Figure 1. Etch rate of NiO and Ga₂O₃ in BCl₃/Ar discharges as a function of ICP power at fixed rf power of 150W. The dc self-bias developed on the electrode is also shown.

Figure 2. Etch rate of (a) NiO and (b) Ga₂O₃ in BCl₃/Ar discharges as a function of rf power at various ICP powers in the range of 200-600W. The dc self-bias developed on the electrode is also shown in (c).

Figure 3. Etch selectivity for NiO over Ga₂O₃ in BCl₃/Ar discharges as a function of rf power for (a) ICP power of 150W and (b) ICP powers in the range 200-600W.

Figure 4. Etch rates for NiO and Ga₂O₃ as a function of $(25 + \text{dc bias})^{0.5}$, which approximates ion energy for (a) different ICP powers or (b) different rf powers.

Figure 5. Survey XPS spectra from (a) NiO and (b) Ga₂O₃ after exposure to the BCl₃/Ar discharge and then subsequent cleaning in either HCl or NH₄OH.

Figure 6. Expanded view of Cl 2p transitions in XPS spectra from (a) NiO and (b) Ga₂O₃ after exposure to the BCl₃/Ar discharge and then subsequent cleaning in either HCl or NH₄OH.











