The Reactive Ion Etching of Transparent Electrodes for Flat Panel Displays Using Ar/Cl[sub 2] Plasmas

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ABSTRACT

Large area flat panel displays require high resolution patterning of transparent and high conductivity metal oxides, but the reliability of standard chemical etch techniques at high resolution is inadequate. Tin oxide (SnO_2) is a viable alternative to standard In_2O_3:Sn (ITO) over large areas but has been ignored due to the lack of a suitable etch process. We have developed an Ar/Cl₂ reactive ion etch process capable of etching 4 μm feature sizes and resolutions of 300 lines per inch with rates of up to 90 nm min⁻¹. Emission spectroscopy showed that atomic chlorine is a strong candidate for the active species and that volatile tin chlorides were generated as etch products. Furthermore, the presence of impurity species, particularly hydrogen, was found to be beneficial to the etch rate. Near etch completion, a dramatic decrease in atomic tin emission was observed along with an increase in Cl emission intensity. The etch rate for tin oxide using Ar/Cl₂ was higher than those obtained for ITO using alcohol-based plasmas without the polymer deposition normally associated with organic gas plasmas. Thus the use Ar/Cl₂ etching of SnO_2 can provide high resolution transparent conductive electrodes that are uniform over a large area.

Introduction

A critical component of flat displays is the transparent electrode, the patterning of which is a primary determinant of the display resolution. With the development of color displays for widespread application the resolution requirements have increased considerably. Traditionally the favored transparent material has been In_2O_3:Sn (ITO) and for low performance displays the tin content has been kept at a minimum, hence sacrificing the conductivity for ease of etching by mineral acids. The higher conductivity specifications now required has led to increased tin incorporation and with it the use of more extreme etch processes such as zinc powder-HCl or electrochemical etching.[1] These methods, although fast, are difficult to control with consequent loss of resolution and fill ratio. Over the past few years initial work has begun on developing vacuum-based plasma processes for dry etching of transparent materials. Methane,[2] acetone, ethanol,[3] methanol,[4] and more recently hydrogen bromide-based[5] plasmas have been used to etch ITO, but in most cases the application was not for flat displays and thus large area considerations such as uniformity, polymer formation, and loading factor were not addressed with any degree of importance. With the advent of dry processing the use of pure tin oxide rather than ITO becomes possible. Tin oxide can be deposited with similar transmittivity and conductivity to ITO but using a low cost atmospheric chemical vapor deposition (CVD) process, which is much more suited to large area uniform coverage, rather than by the vacuum sputtering process used for ITO fabrication. Although Ar and Cl₂ gases have been utilized in the semiconductor industry for a number of years the combination of Ar and Cl₂ gases for plasma etching has, to these authors knowledge, only recently received attention in the scientific literature.[10] A paper by Bassett and Economou[11] deals with the theoretical foundations of dc generated Ar/Cl₂ mixtures but many of the assumptions and conclusions that they draw can be extrapolated with care to the RF case. Our previous work concerning the reactive ion etching (RIE) of tin oxide in Ar/Cl₂ RF plasmas[6-9] characterized etch rates and uniformity against chlorine concentration, power and pattern geometries, where a distinctive loading effect was observed. This work is extended in this paper by introducing optical emission spectroscopy (OES) as a noninvasive diagnostic technique to help develop a more fundamental insight into the etch process.

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Experimental

All the experiments were conducted in a Plasmatech RIE-80 commercial etching machine with water cooled anodized electrodes separated by a distance of 5 cm. The chamber was evacuated to a base pressure of 1 mTorr using a mechanical booster in conjunction with a rotary pump. Gases were fed via VG mass flow controllers to a shower head in the top electrode thus ensuring a uniform flow over the substrate surface; pressure was measured with a 10 Torr VG Baratron. Power from an ENI ACG-5 generator was applied to the lower electrode through a variable impedance matching network with both forward and reflected power being measured. Optical emission was monitored through the Pyrex chamber and taken via a UV fiber to a 0.3 m Monolite™ monochromator with a resolution of <1 nm and a suitably optimized photomultiplier; the spinning diffraction grating enables acquisition of a spectrum every 80 ms. This "snap-shot" of the plasma optical emission can be used to identify the species present in the plasma and also tells us if they are in ionic, molecular, or atomic states. The surface profiling was carried out using a Talystep surface profileometer. Tin oxide was chemically vapor deposited on 3 mm glass substrates which were then thoroughly cleaned using Balzers 1 and 2 cleansing agents; the samples were placed in an ultrasonic bath containing
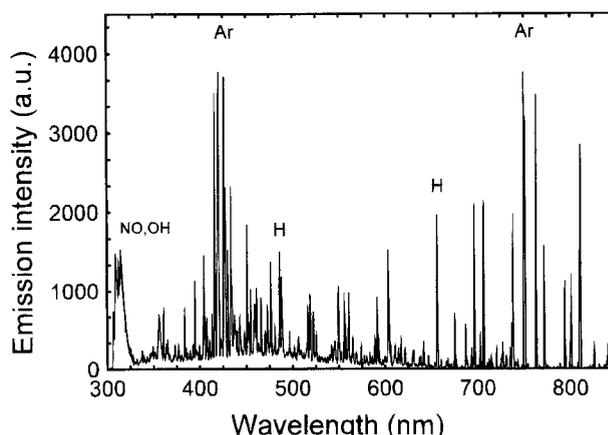

Fig. 1. Optical emission spectrum of a 300 W Ar plasma in the absence of a sample; 5 min pump down.

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deionized water and Decon 90 solution, then cleaned in deionized water, rinsed with acetone, dried with oxygen-free nitrogen, and placed in a 120°C oven. An in-house developed dip-coating technique was used to coat the samples with approximately 1.5 μm of Dynalith OPR-800PG positive photoresist after which they were placed in an 80°C oven for half an hour (prebaking); the substrates were exposed to an uncollimated UV radiation source through a high resolution acetate mask after which the samples were developed and postbaked at 120°C for half an hour. The samples were allowed cool in air for 20 min and were then ready to be etched. Any Ar/Cl$_2$ plasmas used for this work were in the ratio 9:1, *i.e.*, 90%Ar and 10%Cl$_2$ mixtures, whereas the pattern fill ratio consisted of parallel lines with a line density of 50 lines per in. and 50% fill ratio, *i.e.*, the same width of photoresist to tin oxide.

Results

Figure 1 shows the spectrum for a 5 min pump down, 300 W Ar plasma in the absence of a sample. Noticeable are the dominant Ar lines (at 416, 420, 696, 750, and 763.5 nm) and some of the Balmer line series of hydrogen, *e.g.*, H$_\alpha$ (3 → 2) at 656.3 nm, H$_\beta$ (4 → 2) at 486.1 nm. Also present is a band between 305 and 325 nm which is composed of a number of separate sub-bands at 306 nm (OH), 313 nm (CO), with contributions from NO and N$_2$ emission[12,13] indicating the presence of water and nitrogen impurities. It is well known that some water vapor is always present in a vacuum system, no matter how good the pumping techniques used, and in this case a significant decrease in the impurity bands and lines was noticed with increased pump down time. The main outgassing species of unbaked surfaces is usually water which has been adsorbed on the walls and electrodes from the atmosphere on venting with smaller quantities of CO and CO$_2$ also being present. It has been found that when Cl$_2$ is used as a process gas both HCl and Cl$_2$ can cause contamination problems even at ultra-high vacuum.[14] A plasma pretreatment is usually the preferred option. However, this is not possible in the present system as there is no load-lock, and so the sample may be etched or modified by using such a discharge. The desorbed species, mainly water, are impact dissociated leading to a dilution of the plasma with H$^+$ ions, these ions acting in conjunction with Ar$^+$ as the positive charge carriers subsequently bombarding exposed surfaces. If sputtering or sputter etching contributes to the overall etch process then the inclusion of H$_2$O in the chamber may lead to reductions in yields as the H$^+$ ion is so much lighter than the parent gas ion, Ar$^+$. Stern and Caswell[15] found that H$_2$ partial pressures of 5×10^{-7} Torr measurably reduced sputtering rates in Ar discharges. Although the dissociated water dilutes the plasma the H can also reduce the surface SnO$_2$ to Sn and so contribute to the etch process.

Inclusion of a tin oxide sample in the plasma results in spectra identical to the above but with additional Sn lines at 317 and 326 nm of equal intensity irrespective of pump down time. The intensity of the tin lines then decrease as the etch proceeds. The dominant O line at 777 nm cannot be detected, possibly due to the dynamic range of the optical detection system being severely curtailed at the higher wavelengths. The H lines and the UV band associated with OH and NO actually increased with etch time for long pump down times even though the sample had been under vacuum for 2 h. The average etch rate for long pump down times (≥24 h), 12 nm/min, was slightly greater, by 9%, than that for the short pump down case. The etch rate of the photoresist is difficult to measure accurately but is approximately three times that of the tin oxide.

Ar/Cl$_2$ spectra were obtained for short and long pump down time with and without tin oxide samples. Similar impurity lines and bands, as found with argon only but with lower intensity, were observed in the short pump down case, and these increased when a sample was introduced. For pump down times greater than 2 h such impurities were not detected. The chlorine species observed were Cl lines, with the dominant ones being at 725.7 and 754 nm,
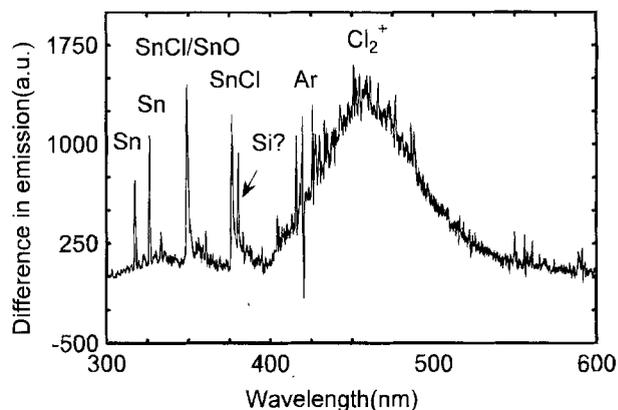

Fig. 2. Difference between the spectrum in the presence of a sample being etched in 300 W Ar/Cl$_2$ and the spectrum in the absence of a sample; 24 h pump down.

and a Cl$^+$ line at 480 nm. A blue band in the 400 to 600 nm range, normally attributed to the Cl$_2^-$ $^2\Pi$ − $^2\Pi$ transistion, was also present for all configurations but was significantly enhanced for long pump downs with the sample in place. Figure 2 is the result of the subtraction of a 24 h pump down Ar/Cl$_2$ spectrum with no sample from the corresponding long pump down spectrum which includes a tin oxide sample being etched; the above mentioned differences can be clearly seen. Tin-based etch products are visible as Sn lines at 317 nm, when not obscured by the impurity bandedge, and 326 nm, while a SnCl band is observed at 375.8 nm. The band at 349 nm may be attributed to either SnO (348.4 nm) or SnCl (348.8 nm) [12] and since it is also present in the 100% Ar plasma spectrum, the former is more likely. However, sidewall desorption of residual chlorine-based species, in an Ar plasma, cannot be ruled out. The intensities of the Sn, SnO/SnCl products, in Ar/Cl$_2$, are significantly greater for long pump down times yet the average etch rate, 25 nm/min, is approximately half that obtained after a short pump down. Generally, for Ar and Ar/Cl$_2$, the impurity bands, the Sn-based species lines and, for Ar/Cl$_2$, the Cl$_2^-$ band are constant or decrease as the etch progresses. However, for the short pump down Ar/Cl$_2$ case, the Sn, SnCl, SnCl/SnO, and Cl$_2^-$ all increase to a maximum as the etch proceeds before falling as the etch approaches its endpoint.

Figure 3 shows the behavior of the Sn (326 nm) line measured with a Kratos GM252 fixed grating monochromator and a Hamamatsu 1P28 photomultiplier during etching in Ar/Cl$_2$ plasmas for short (5 min) and long (2 h) pump down times, respectively. Immediately obvious are the rise time
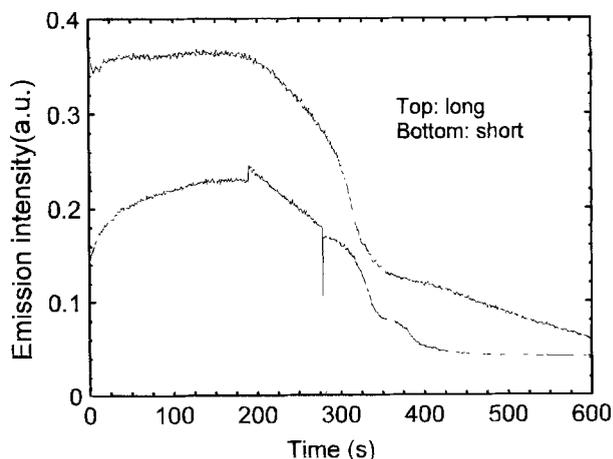

Fig. 3. Behavior of the Sn (326 nm) emission line as etch proceeds in a 300 W Ar/Cl$_2$ plasma; top trace corresponds to 2 h pump down, bottom trace is for a 5 min pump down.
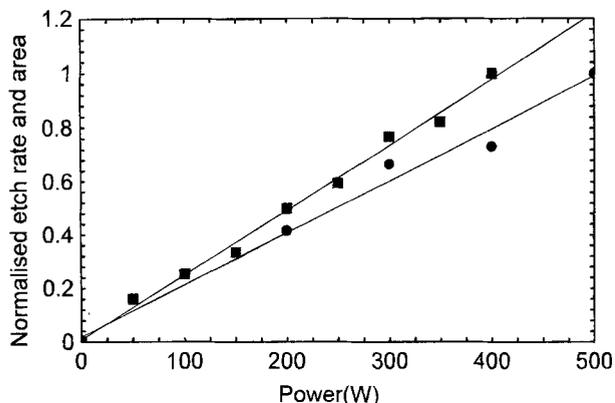
Fig. 4. Normalized area under the curves as in Fig. 3. and normalized etch rate of tin oxide film measured with Talystep against input power in Ar/Cl$_2$ plasma against input power.

for the short pump down case, the emission then peaks and decreases to a "background" level at the end of the etch. This emission line behavior with time has also been observed in the etching of InP and GaAs [16] in Cl$_2$. For the long pump down there is no "dead time," and the emission is approximately constant with time, decreasing again to a background level. Similar trends are observed in the dc bias against etch time with the voltage decaying initially to a plateau and then rising again after the time corresponding to the knee in the above curve.

Greene[13] has detailed the use of electronic integration of the emission intensity from a sputtered species with time as an indication of the total amounts of material deposited at the substrate; for the present case some useful information can be obtained if one tentatively takes the area under the curve as being an indication of the relative amount of Sn removed during etching. Figure 4 shows the normalized area under the Sn(t) curve for different unpatterned substrates at different powers. This shows a linear increase in etch rate with power and compares well with the measured etch rate. However, it is clear that a difference in emission mechanism occurs between short and long pump downs, and thus the use of actual intensities to compare between short and long pumpdown etch rates is not valid.

Substrate temperature is a very important process parameter [4,5] especially when volatile etch products are being produced. The temperature was monitored by venting the chamber, and using an infrared sensor. In Fig. 5 the temperature-etch power profile is given for a 8 min etch in Ar/Cl$_2$. The trend is as expected with increasing temperature at higher process powers being due to the increased number and energy of ions impinging on the substrate as
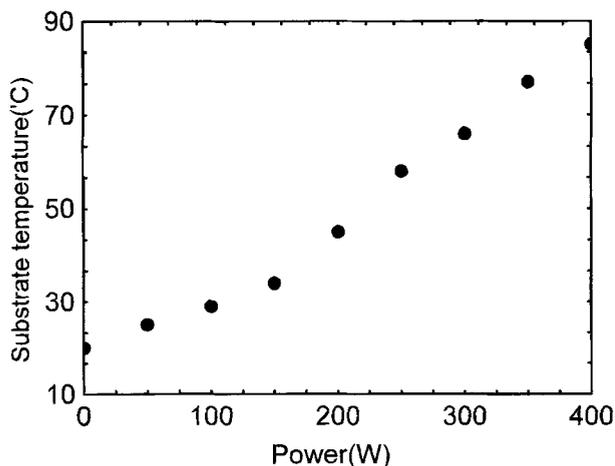

Fig. 5. Substrate temperature taken shortly after etch against input power.

well as the increased Cl recombination, the atomic chlorine recombination reaction being exothermic by approximately 1.1 eV. The actual trend is probably steeper at higher powers but due to the rapid cooling on venting at these temperatures the measurements are distorted. The temperatures were a few degrees lower in each case when the pump down time was only a few minutes, this being due to the fact that bombarding H$^+$ ions will impart less momentum to the substrate and hence generate less heat. The temperature of a Si substrate during Ar plasma etching is known to rise exponentially and then saturate after a few minutes,[17] but silicon is a much better conductor of heat than the 3 mm glass used here, implying that the temperature rise during the etching of tin oxide probably takes place over a much smaller time scale. The substrate temperature is therefore roughly constant throughout the etch and changes in reaction product evaporation rates can be neglected. This is in agreement with previous work [6] which details an approximately linear etch rate with time at 10% Cl$_2$.

The etch rate increases from 12 nm/min at 0% Cl$_2$ to ~30 nm/min for small additions (~5%) of Cl$_2$. Further increases in etch rate occur with Cl$_2$ but at ~20% Cl$_2$ the increase tends to saturate at approximately 60 nm/min. We have performed a limited number of runs at 50% and 100% Cl$_2$ without any increase in etch rate. In pristine Cl$_2$ plasmas, the Cl dissociation fraction has been reported to range from 0.1 [18] to 0.6, [19] however, there are many Cl generation processes in Ar/Cl$_2$ plasmas including electron impact dissociation of Cl$_2$, Ar metastable quenching by Cl$_2$, and electron dissociative attachment to Cl$_2$ to form Cl$^-$ and Cl, and so the fraction of atomic chlorine present in the system may be considerably higher than that for pure Cl$_2$. Figure 6a shows the variation with percentage chlorine in Cl, Cl$^+$, and Cl$_2^+$ emission intensities at 725.7, 480, and 408 nm, respectively, keeping the total pressure constant. Also shown is the etch rate variation with percent Cl$_2$, and there is excellent agreement between the rate, the Cl and Cl$^+$ emission suggesting a strong correlation between the atomic chlorine concentration and/or Cl$^+$ and etch rate; statistical analysis shows a cubed root relationship between the etch rate and the percent Cl$_2$ (goodness of fit >0.98 for Cl and Cl$^+$, >0.92 for etch rate). After an initial rise in Cl$_2^+$ emission it remains relatively constant which implies that the molecular ion does not play a major role in the etch process, however, the role of the Cl$_2^+$ ion needs further investigation. Figure 6b shows the relation between the Sn emission line at 317 nm and the atomic Cl line at 725.7 nm with time, a slight increase in the Cl intensity is observed at the knee in the Sn emission. This suggests that the atomic chlorine is no longer being consumed at the surface, i.e., etching has all but ceased.

Discussion

We have used OES analysis in an attempt to obtain further insight into the etching of SnO$_2$ within a realistic etching environment. Excitation followed by emission of radiation may arise due to a number of different collision processes: (i) electron-atom collisions, (ii) ion (e.g., Ar$^+$, Cl$_2^+$) atom collisions in or near the sheath, (iii) metastable-atom collisions, (iv) electron impact dissociation, and (v) recombination on surfaces. For instance, if the excitation is due to electron-atom/molecule collisions then the intensity, I, of a spectral line emitted by a plasma is strongly dependent on the electron energy distribution function, i.e.

$$I \propto n_o \int_0^\infty \sigma \ (\epsilon) f_e(\epsilon) \ d\epsilon \qquad [1]$$

where n_o is the density of the atomic or molecular species in the electronic ground state, ϵ is the electron energy, $\sigma(\epsilon)$ is the electron excitation cross section, and n_e is the electron number density. The emission intensity is seen to be a very sensitive function of plasma parameters. Care must be taken with regard to interpreting the emission plots as not only are they representative of the amount of tin removed but also the amount of excited Sn in the discharge at any
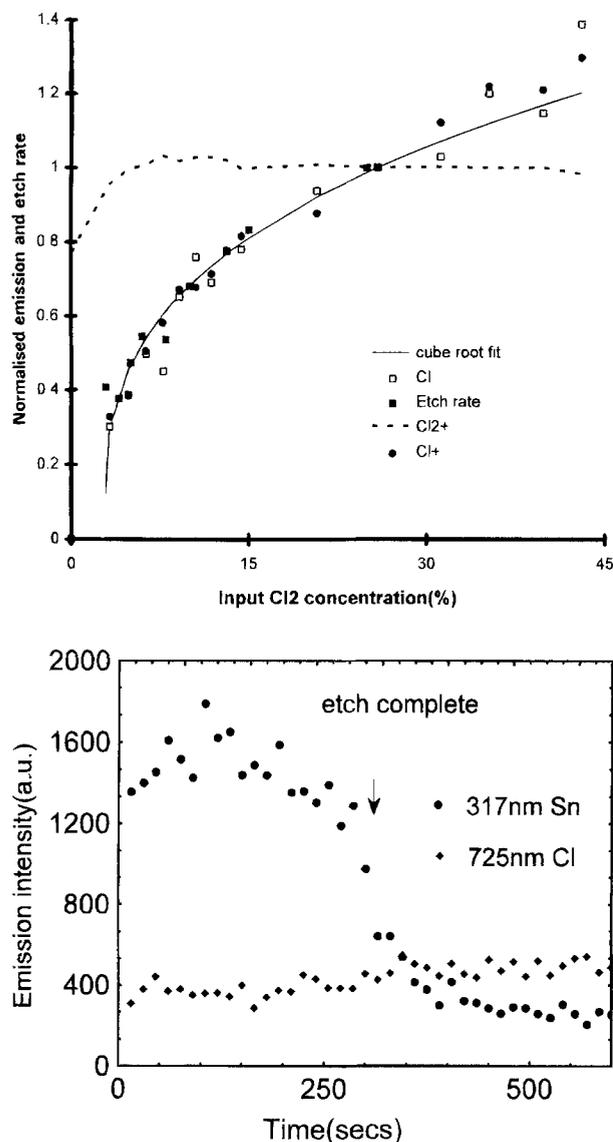
Fig. 6 (a, top). Etch rate of tin oxide, Cl (725 nm), Cl⁺ (480 nm) and Cl⁺² (408 nm) emission intensities with chlorine concentration at fixed total pressure in 300 W Ar/Cl₂ plasma. All data has been normalised to 25% Cl₂. (b, bottom) Time dependence of Sn (326 nm) and Cl (725 nm) emission intensities as etch proceeds.

particular time. The limitations of OES are often overcome by using actinometry, but it is not a suitable diagnostic in the present case as it relies on electron impact excitation of the ground state chlorine atom being the only source of emission. Chlorine discharges have been studied using small amounts, typically 5%, of argon as the actinometric gas and reasonable results are obtained as long as the emission is taken from the plasma bulk and is not adjacent to the sheaths. Since the typical mix ratio is 90% Ar:10% Cl_2 in our case, then the influence on the electron energy distribution function cannot be ruled out and Bassett *et al.*[11] have shown that Ar metastables can have a pronounced effect on the generation of excited atomic chlorine.

Polycrystalline SnO_2 is rutile with [200], [110], [101], [100], [211], [310], and [301] surface planes, depending on the fabrication process.[20] The likely structure encountered in this work is a partially hydroxylated [200] plane in SnO_2. There are a number of possible reaction sites present, *i.e.*,]-OH groups,]-O,]-O-[, and bare metal tin sites on the surface than can accept a pair of electrons; the ratio depends strongly on the history especially the thermal history, of the sample.[21] The surface is quite strongly oxidizing in nature with any oxygen deficiency being quickly replenished by the chemisorption of atmospheric oxygen. As detailed in the section on experimental procedure the tin ox-

ide samples are thoroughly cleaned and heated at 120°C for 30 min prior to etching, however, the samples are then let cool down in air, and so it is possible that they re-adsorb the OH groups. A fraction of these OH groups are removed when the sample is heated in vacuum thus altering the surface chemistry of the substrate.

With short pump down times and low vacuum, the presence of atmospheric impurities and the re-entry of adsorbed etch products from previous runs is to be expected. For a 100% Ar plasma, there is little difference in the impurity band intensities for long (>2 h) and short pump down times, with or without sample. The unavoidable presence of water in the chamber is most likely enhanced due to trapping by hydrophilic $SnCl_x$ etch products adsorbed onto the walls forming $SnCl_x \cdot n\,H_2O$. This is then difficult to evacuate even with long pump downs. However, once etching commences, the increased emission, observed with the long pump down, indicates enhanced desorption due to plasma bombardment. That the etch rate is slightly higher for the longer pump down is evidence that water-based impurities do not have deleterious effects upon etching and may, in fact, be beneficial.

It is known[22,23] that the mechanism of SnO_2 removal by high energy Ar^+ bombardment proceeds via preferential sputtering of oxygen leading to the formation of SnO, which disproportionates, slowly, via the reaction $2\,SnO \rightarrow Sn + SnO_2$. Direct sputtering of Sn^0 and possibly SnO then occurs. Major *et al.*[24] and Gianetti *et al.*[25] have found reduction of the SnO_2 surface to SnO and free metal following treatment in a hydrogen plasma, the former used a low energy H_2 plasma where the samples were placed on the grounded electrode, hence the sputtering component was considerably reduced. Given the high energies or densities involved and the operation at ultra high vacuum (UHV), such results are of limited application in our case. However, the possible creation of Sn^0 by Ar^+ bombardment and enhanced reduction with hydrogen is important for the Ar/Cl_2 process since free chlorine will readily form volatile products with free tin. Thus a fuller investigation of the Ar and Ar-hydrogen etch mechanisms in a representative plasma environment is required.

The addition of Cl_2 to Ar dramatically increases the etch rate, *e.g.*, from 12 to 30 nm/min with 5% Cl_2: the rate continues to increase before approaching saturation at approximately 20% Cl_2 with values of 60 nm/min (50% fill ratio). The OES intensities for short pump down plasmas show a strong correlation between etch rate and Cl/Cl^+ species, Fig. 6a, yet, despite its expected dominance, there is little correlation between rate and Cl_2^+. For all situations, except the long pump down plasma, the Cl_2^+ band intensity, from 400 to 600 nm, was small but increased significantly after a long pump down with sample, Fig. 2. The magnitude of the Sn lines had also increased and both species emissions decreased with etch time. This is a fairly clear indication that the observed Cl_2^+ is a by-product of etching with $SnCl_x$ volatile or sputtered fragments dissociating in the bulk plasma to give excited Sn and Cl_2^+. OES intensities, from plasmas with a large number of possible excitation mechanisms, do not necessarily indicate absolute species concentration and this is clear from comparison of short and long pump down tin species emission, which is greater in the latter, yet a much lower etch rate is observed. This fact, in conjunction with the Cl_2^+ intensities, indicates a difference in etch mechanism between the two pump down regimes. A further difference is the absence of any impurity emission in the long pump down plasma. It is not obvious why the trend here is opposite to that of the 100% Ar plasma, where plasma bombardment is thought to enhance desorption of sidewall impurity species. Nevertheless, the reduction of etch rate in the absence of impurities is evidence of the importance of hydrogen for the reduction of the surface to free tin, which would more readily form volatile choride species.

The residence time and hence the probability of dissociation/emission of desorbed species within the plasma would depend on their volatility. Thus, by implication, the long

pump down spectra indicate that significant lower volatility species are being removed. Gerlach-Meyer *et al.*[26] have shown that, for the Si-fluorine and Si-chlorine systems, ion-enhanced chemisorption/desorption proceeds via the production of natural volatile species whereas the production of involatiles, which in our case are $SnCl$, $SnCl_3$, or clusters thereof, normally occurs via direct sputtering. The enthalpies of formation, ΔH_f, for $SnCl_2$, $SnCl_4$, and $SnCl_2 \cdot 2H_2O$ are -349.4, -544.7, and -945.16 kJ mol^{-1},[27] respectively, with increasing negative values indicating a greater likelihood that the reaction will proceed; the effect of the plasma environment will of course complicate matters but the trends shown above will be similar. $SnCl_2 \cdot 2H_2O$ has the lowest enthalpy but decomposes at 37°C, well below the substrate temperature during etching. $SnCl_2$, with a melting point of 246°C, has a much lower volatility than $SnCl_4$ (mp = -33°C) but, using energy dispersive x-ray analysis (EDS), it has been detected as the predominant sidewall condensate. Note that such a condensate will trap water, on exposure to atmosphere, forming $SnCl_2 \cdot 2H_2O$.

A complete understanding of the etch mechanism requires a detailed analysis of the Ar/Cl_2 plasma, the physical and chemical reactions at the SnO_2 surface, and the effect of trace impurities on these two systems. Over 30 different reactions have been detailed in Ar/Cl_2 dc plasmas,[11] and such species will contribute to ion-enhanced surface reactions and ion-mixing as well as direct physical sputtering. Ion-enhancement is a low threshold process and a single ion impact can influence the surface over a substantial area about that point of impact, causing adsorption/desorption of weakly bonded species.[26] Ion bombardment of the surface can also create defects and interstitials and at the same time induce mixing of adsorbed chlorine into the surface lattice where some may react with interstitials to form low binding energy tin-chlorine molecular products. In the Si-Cl_2-Ar system, a single Ar$^+$ ion can mix up to 4 Cl atoms.[28] Etching of SnO_2, in common with other metal oxides, is difficult. Comparable SiO_2 rates are possible with much lower power densities. Furthermore, a strong loading effect has been observed,[8] thus indicating the Ar/Cl_2 process to be at the limits of its etching capability. It is not surprising therefore that small quantities of impurities may significantly affect the etch rate, by critically modifying the plasma or surface chemistry.

Conclusions and Summary

The use of Ar/Cl_2-based reactive ion etching has been shown to be a viable process for the etching of SnO_2 with etch rates up to 60 nm/min at 50% fill ratio. Development of the process to enhance the rate, without loss of uniformity, requires a fuller understanding of both the reactive and nonreactive ion/neutral surface reactions and the bulk plasma, both of which are complex systems, little understood, and with large parameter spaces. OES analysis has indicated the significance of impurity species (H, N, NO, OH) in relation to the etch rate and this is thought to be due to enhanced reduction of the surface by hydrogen. However it is not clear how hydrogen species will effect the characteristics of the plasma itself. OES has also shown a stronger correlation between Cl/Cl$^+$ species and etch rate compared to the dominant Cl_2^+ ion. A more detailed investigation of the separate argon, argon-hydrogen, chlorine-hydrogen, and argon-chlorine-hydrogen systems is required therefore, before a definitive etch mechanism can be determined.

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