Patterning of metal oxide transparent electrodes for flat panel displays using an Ar/Cl_2 based reactive ion etch process.

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We have developed an Ar/Cl_2 reactive ion etch process, capable of producing etch rates up to 90nm min^{-1} uniformly over a substrate area of 130cm^2, and have investigated some of the underlying mechanisms involved with this relatively uncommon gas mixture and its interaction with the tin oxide. OES has indicated that atomic chlorine is a strong candidate for the active species and that volatile tin chlorides were generated as etch products. This finding was endorsed by EDS which showed $SnCl_x$ (x=2,4) on the chamber walls. End point detection demonstrated an increase in the Cl emission line intensity coupled with a sudden decrease in atomic tin emission near etch completion. OES was also used to detect water and nitrogen impurities which can lead to plasma dilution and so decrease process efficiency.

Introduction and Experimental

Tin oxide (SnO_2) is a viable alternative to Indium Tin Oxide (In_2O_3:Sn) as the front electrode in flat panel displays since it can be deposited over very large areas using atmospheric CVD. To date it has been largely ignored due to the lack of a suitable etch process. Glass substrates with a CVD layer of doped tin oxide (300-400nm, 6-10Ω/□) were used throughout. The substrates were cleaned in an ultrasonic bath containing hot, de-ionised (DI) water and Decon 90 solution, followed by a DI water rinse. This was followed by acetone rinse, blow dry (in oxygen free nitrogen) and oven dry at 120°C for 30 minutes. Dynalith OPR-800PG photoresist was dip-coated to 1.5μm average thickness and then prebaked at 80°C for 30 minutes. A high resolution acetate mask was used in conjunction with an uncollimated UV source to pattern the photoresist followed by a 30 minute postbake at 120°C and 20 minutes cooling in air. All etching was carried out in a Plasmatech RIE-80 with an ultimate base pressure of approximately 1mTorr. Optical emission through the chamber wall was taken via a UV fibre to a 0.3m Monolite monochromator with a resolution of <1nm coupled to a suitably chosen photomultiplier. RF power at 13.56MHz was applied via an impedance matching unit and blocking capacitor to the lower electrode which was surrounded by a dark space shield. Etch rates were measured using a Talystep surface profileometer and the surface topography studied with a Burleigh Personal Surface Probe Microscope used in its atomic force microscopy (AFM) mode.

Results and discussion

Fig. 1 shows the emission spectrum of a 300W Ar plasma with no sample for a short (5 minutes) pumpdown time. As expected, one can see Ar lines, e.g. 416nm, 696nm and 750nm but there are also some lines and bands corresponding to impurities that have not yet been evacuated from the chamber such as H_2O and N_2. For instance the lines at 656.3nm and 486.1nm correspond to $H_\alpha(3\rightarrow2)$ and $H_\beta(4\rightarrow2)$ respectively, and the band between 305nm and 325nm is composed of a number of sub-bands at 306nm(OH) and 313nm(CO) [1] along with contributions from NO and N_2. These impurity features decrease with increasing pumpdown time. The species concerned are probably desorbed from the walls and subsequently broken into fragments and perhaps ionised. Tin oxide adsorbs atmospheric water mainly at steps and defects and is often dissociated, i.e. $H_2O + O^{2-}\rightarrow 2OH^-$: a common reaction with polycrystalline SnO_2 leading to a covering of the exposed surface in hydroxyl groups [2]. The H^+ ions can also dilute the plasma and if sputtering is an important part of the process they can act as the positive charge carriers and bombard the substrate on the driven electrode. H^+ ions are much lighter than Ar^+ ions and so sputtering efficiency and sputtering yields are expected to drop. However, H and CO atoms and ions may reduce the surface, thus contributing to the etch process.

With a sample in place for a short pumpdown time and using a pure Ar etch, the resulting spectrum shows emission from the Sn atom at 317nm and 326nm and also a band that corresponds to SnO at 349nm. When a sample is etched in Ar/10%Cl_2 for a 5 minute pump down the Sn lines are also evident. In addition to the Sn lines SnCl bands at approximately 349nm and 376nm are observed although the band at 349nm may also be due to SnO (348.4nm) as opposed to 348.8nm for SnCl. Fig. 2 is the result of the subtraction of the spectrum of a long pumpdown Ar/Cl_2 plasma in the absence of a sample from the spectrum under similar process conditions but with a sample present.. A strong blue band in the 400-600nm range is visible. This band can be attributed to the $^2\Pi$-$^2\Pi$ transition in the molecular chlorine ion, i.e. Cl^+_2 [1]. The presence of this band occurs only with long pumpdown and a sample in place, thus implying that it arises due to dissociation of $SnCl_x$ volatiles in the absence of OH/H_2O impurities. Since $SnCl_x$ (x=1,2,4) is hydrophilic, it is possible that the presence of such impurities leads to the formation of $SnCl_x.nH_2O$ which remains trapped at the primary impurity source, namely the chamber walls. Energy Dispersive Spectroscopy (EDS) analysis of the material deposited, after short pumpdown, onto the chamber walls, indicated $SnCl_x$ (x=2,4) with the less volatile chloride (x=2) predominant [3]. In the absence of OH/H_2O impurities these etch products can re-enter the plasma and undergo fragmentation and excitational collisions with electrons and ions.

It is well known that optical emission is possible via a number of pathways, e.g. electron impact excitation, recombination on surfaces and electron impact dissociation but spectral line intensity is a very sensitive function of plasma parameters and great care must be taken in their interpretation , for example, the intensity of the Sn line is not a true representation of the amount of tin removed from the substrate but corresponds to the amount of excited tin in the discharge at that time. Fig. 3 shows the behaviour of the Sn (326nm) line with etch time for long and short pump down times in a 300W Ar/Cl_2 plasma. The latter has an initial rise time that probably corresponds to the removal of the surface OH groups, and drops to a background level at or near etch completion. There is a corresponding rise in the emission from atomic chlorine, suggesting that Cl has been used during the etch. Similar emission line behaviour to that in Fig. 3 has been observed in the etching of InP and GaAs [4] in Cl_2.

Fig. 4 shows the variation in Cl, Cl^+ and Cl^+_2 emission intensities at 725.7nm, 480nm and 408nm repectively with increasing Cl_2 concentration in the discharge, at constant total pressure. Also shown is the etch rate variation and there is excellent agreement between the rate, the Cl and Cl^+ emission which suggests a strong correlation between the atomic chlorine concentration and/or Cl^+ concentration and etch rate. The goodness of fit is at least 0.98 for Cl and Cl^+ and 0.92 for the etch rate. The temperature of samples etched in Ar/Cl_2 shows a linear increase with power up to 400W with a maximum observed value of 85°C. The measurements were taken approximately 60 seconds after the plasma had been extinguished and the system vented with nitrogen. As expected the temperature rises with increasing power due to increased ion bombardment energies and fluxes. The magnitude of the rise in temperature is due to the thermally insulating glass (3mm) substrates used and is significant given the volatility of the etch products (b.p. $SnCl_4$: 114.1°C). The temperatures are a few degrees higher in the long pump down case as there is no longer dilution due to desorbed water/hydrogen.

On the surface of cassiterite, the mineral form of SnO_2, the bridging O ions can be easily removed and replaced, depending on the treatment, e.g. heating, ion bombardment [2,5]. Preliminary XRD analysis shows the dominant crystal faces to be 110, 200 and possibly 211. There appears to be some preferential etching in Ar plasmas along the 200 face with no apparent trend in the 110 face. The surface topography was measured using AFM and the tin oxide grain size analysed statistically. Fig. 5 shows the root mean square of the peak height in a 7μm^2 area for each sample with the data has been normalised to the value at 150W. The grain size increased in area up to 150W after which it decreased. The samples, initially transparent, become increasingly brown after 150W indicating some kind of surface change. This may be due to the incident Ar^+ reducing the surface [5] by removing the O^{2-}, thus leaving two electrons behind, i.e. $Sn^{4+}O^{2-}_2 + Ar^+ \rightarrow Sn^{2+}O^{2-} + Ar^+ + O\uparrow$. The top layer then consists of SnO (which is usually black in nature) mixed with various defect sites. The OH/H_2O impurities may also contribute by reacting at these defect sites producing tin hydrides and oxides. The discoloured films can be made clear again by heating to above approximately 300°C in air, suggesting that the surface has become reoxidised, whereas heating the brown samples in an Ar atmosphere has very little effect on the colour.

Depending on the applied power and the chamber pressure, the incident positive ions may attain energies commensurate with the DC bias and so can sputter etch the surface groups, e.g. OH and O, and subsequently impact dissociate or weaken the SnO_2 and SnO bonds (Sn-O 557kJmol^{-1}). Atomic or molecular chlorine that has diffused to the surface will then form volatile products, $SnCl_x$ (x=1,2,4), their removal being hastened by ion bombardment. Another important source of Cl at the surface may be due to asymmetric charge exchange collisions whereby a Cl_2 molecule on the plasma bulk side of the sheath is impacted by an energetic positive ion, charge exchange occurs and the incident ion is converted to a slow (approximately thermal) neutral. The original Cl_2 either fragments into two energetic atoms or is ionised, these fragments impinge on the surface in an excited state and so are highly reactive. The enthalpies of formation, ΔH_f, for $SnCl_2$, $SnCl_4$ and $SnCl_2.2H_2O$ are -349.4 kJmol^{-1}, -544.7 kJmol^{-1} and -945.16 kJmol^{-1} [6] respectively with increasing negative values indicating a greater likelihood that the reaction will proceed.

Molecular chlorine ions, Cl^+_2, are also likely to be involved in the etch process although their significance has not yet been quantified. OES demonstrates no correlation between the Cl^+_2 signal and the etch rate although it should be remembered that Cl^+_2 is the dominant chlorine ion at 13.56MHz and these ions can be chemisorbed on the surface where they react with the tin oxide/tin to produce the volatile products. Mayer *et al.* [7] studied the etching of Si and SiO_2 using beams of reactive gas ions and found that chemical reactions due to ions are important over a wide energy range but chemisorption is the dominant mechanism at low energies whereas momentum transfer becomes more important as the incident ion energy increases. The energy of the incident ion (Ar^+, Cl^+_2) could be dissipated over a relatively large area of the substrate surface and this extra energy may excite existing reaction products e.g. $Cl_2+SnCl_3^* \rightarrow SnCl_4\uparrow+Cl$. This process can be termed an ion-enhanced chemical reaction and is related to the amount of Cl on the surface which is related to the Cl_2 and ion fluxes. A mechanism has been postulated by Sugino *et al.* [8] for the etching of Si through a native oxide using Cl radicals. In the case of tin oxide the atomic or molecular chlorine diffuse to the surface and react with exposed sites, e.g. Sn or SnOH, forming volatile compounds that evaporate and leave another site available for a similar reaction to occur i.e. a type of localised etching takes place. A clearway or channel is created locally for any reactive species to 'burrow' in to the bulk and for the resultant product to be desorbed.

Conclusions and Summary

Optical emission spectroscopy has been used to gain insight into possible etch mechanisms for tin oxide in an Ar/Cl_2 reactive ion etching environment. Impurities such as water and nitrogen can be detected, these being greatly diminished the longer the pump down time. Atomic chlorine is thought to play a major role as there is a strong correlation between etch rate and Cl emission. A number of possible etch mechanisms are given with positive ion assisted removal of volatile chlorides being the most likely candidate, with other mechanisms occurring in tandem but to a lesser degree. Monitoring of Sn lines during etching can also be useful but care must be taken as the emission intensities reflect not only the amount of tin being removed from the substrate but also the excitation methods. Deposition of photoresist and hydrocarbons is not a problem with Ar/Cl_2 plasmas and resolutions of 300 lines per inch are achievable with 4μm feature sizes. Thus we have established the viability of reactive ion etching as a suitable technique for patterning high resolution transparent flat display front electrode arrays with high etch rates and good uniformity over a large area.

References

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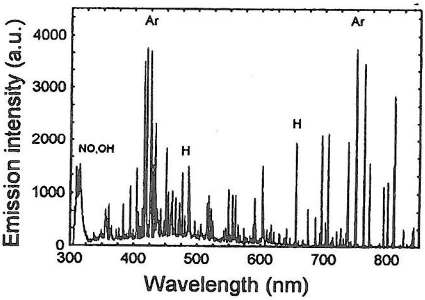

Fig. 1 Optical emission from a 300W Ar plasma in the absence of a sample; 5 min. pumpdown.

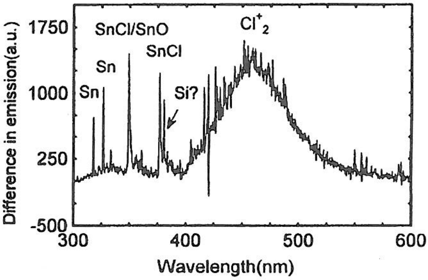

Fig. 2 Difference between the spectrum of a sample being etched in Ar/Cl_2 and the spectrum in the absence of a sample; 2 hour pumpdown.

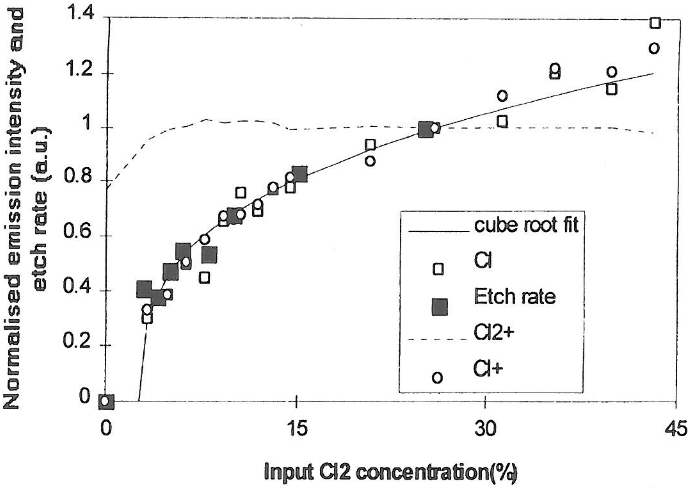

Fig. 4 Etch rate of SnO_2, Cl (725nm), Cl^+ (480nm) and Cl^+_2 (408nm) emission lines versus %Cl_2 at fixed pressure in Ar/Cl_2. Data normalised to 25%Cl_2.

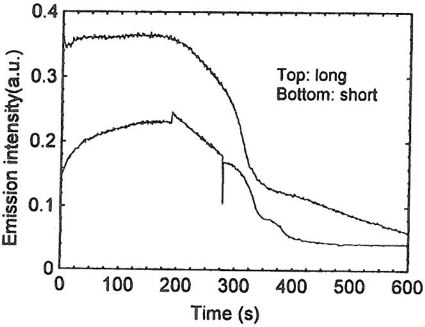

Fig. 3 Behaviour of Sn (326nm) as the etch proceeds in Ar/Cl_2; top corresponds to 2 hour pumpdown and bottom to 5 minute pumpdown.

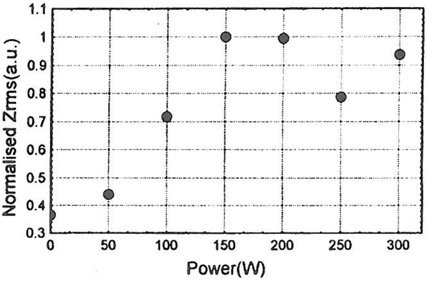

Fig. 5 Root mean square peak height of grains for tin oxide samples etched in Ar against power.