Dry etching characteristics of amorphous As$_2$S$_3$ film in CHF$_3$ plasma

Duk-Yong Choi, a Steve Madden, Andrei Rode, Rongping Wang, and Barry Luther-Davies

Centre for Ultra-High Bandwidth Devices and Optical Systems, Laser Physics Centre, Research School of Physical Science and Engineering, The Australian National University, Canberra, Australian Capital Territory 0200, Australia

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The authors describe the dry etching characteristics of amorphous As$_2$S$_3$ films in CHF$_3$ plasma and the development of an optimized fabrication process for compact waveguides. The observed etching behavior is due to the relative densities of fluorine atoms, polymer precursors, and ions in the plasma which are controlled by the process parameters. In particular, the flow rate of the CHF$_3$ gas has a significant influence on the etched profile and surface roughness as well as the etch rate of the As$_2$S$_3$. The profile evolves from isotropic to vertical with the flow rate due to passivation by increasing polymer deposition on the sidewalls. Such passivation also helps achieve smooth sidewalls because it inhibits differential etching between the phases in the inherently phase-separated As$_2$S$_3$ film, which otherwise results in a grainy and rough etched surface. At the highest flow rate, however, excessive polymer deposition occurs and this results in positive-sloped sidewall and grassy etched surface due to micromasking. © 2008 American Institute of Physics.

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I. INTRODUCTION

A chalcogenide glass (ChG) is one containing the chalcogen elements (S, Se, or Te) as a substantial constituent covalently bonded to network forming elements such as Ge, As, Sb, or Si. ChG films are widely used in data storage media (DVD-R) and nonvolatile random access memories. They are also emerging as good candidates for integrated nonlinear optic devices due to their high optical nonlinearities and low linear and nonlinear losses. Recently, they have been also applied as chemical or biosensors utilizing their wide transparency particularly in the mid-IR where most chemicals and biological toxins have their spectral fingerprints.

The laser-writing technique, which exploits refractive index changes induced by the photostructural effect in ChGs exposed to light near their band edges, has been frequently used to produce waveguides in thin ChG films. These photoinduced refractive index changes are, however, unstable because the bond structure of the glass can relax at room temperature and, therefore, this approach is unsuitable for practical devices. To overcome this issue, waveguides can be fabricated by etching the film to create ridge or rib-type waveguides. Wet etching has been applied with NH$_4$OH as an etchant; however, serious undercutting of the pattern always occurs due to the isotropic nature of the chemical process, and this makes the control of waveguide dimensions difficult. We, therefore, have adopted dry etching as the preferred method for fabricating As$_2$S$_3$ waveguides.

Although we obtained nearly vertical etched profiles using CF$_4$–O$_2$ plasma, the high oxygen content in the plasma caused other problems. For instance, poor etch selectivity to photoresist (PR) led to a large etch bias (~0.8 μm loss in pattern width for a 1 μm etch depth). Moreover, phase separation in the film caused the etched surface to roughen due to the strong chemical etching nature of plasma containing high numbers of fluorine radicals. Consequently it was difficult to fabricate waveguides with small mode areas (~1 μm$^2$) required to obtain nonlinear optical devices operating at very low powers (<1 W). Therefore improved plasma chemistries are desirable.

In this study we investigated the etch characteristics [the etch rate (ER), the selectivity, the edge profile, and the etched surface roughness] of amorphous As$_2$S$_3$ films in CHF$_3$ plasma and identified suitable patterning conditions to obtain waveguides with dimension in the micron range. The chemical reaction with fluorine radicals remains the main removal mechanism for etching As$_2$S$_3$ films. The change from CF$_4$ to CHF$_3$, however, reduced PR mask erosion due to enhanced polymer deposition so that high etch selectivity and small etch bias was achieved during patterning. In particular the CHF$_3$ flow rate significantly affected all the observed etching behavior. The relative densities of fluorines, polymer precursors, and ions in the plasma are the key parameters which determine the morphology of the etched profiles, the ERs, and the appearance of micromasking.

II. EXPERIMENTAL

As$_2$S$_3$ films were deposited by thermal evaporation on thermally oxidized silicon wafers in a chamber evacuated to $2 \times 10^{-7}$ torr. Deposition occurred with the source to substrate distance of ~40 cm at a rate typically of ~0.2–0.3 nm/s. The nominal thickness of the As$_2$S$_3$ was 2.5 μm. A bottom antireflective coating (BARC) (XHiRC-16 from Brewer Science) was coated onto the As$_2$S$_3$ film at a spin speed of 5000 rpm and cured at 115 °C for 2 min on a hot plate. PR patterns were produced on the BARC using contact photolithography (MA6 from Suss Mi-
croTec) at 365 nm using a high-resolution resist (Clariant AZ MiR701). An inductively coupled plasma reactive ion etching system (Plasmalab100 from Oxford Instruments) was used to etch the BARC and As$_2$S$_3$. The BARC was etched in oxygen plasma with the addition of small amounts of argon and CHF$_3$, while pure CHF$_3$ was utilized to pattern the As$_2$S$_3$ film. The ERs of the films and PR were measured in situ by a laser interferometer (D-205 Digilem from Jovin Yvon-Sofie). We used $-15 \times 15$ mm$^2$ sized As$_2$S$_3$ samples for the experiments. The design of experiments (DOEs) method was applied to investigate systematically the etch characteristics of the As$_2$S$_3$ in CHF$_3$ plasma and to determine the best conditions for etching. A scanning electron microscope (SEM) (Hitachi S4500) was used to observe the etched profile and sidewall morphology. X-ray photoelectron spectroscopy (XPS) was used to study the chemical bonding of C 1$s$ and the existence of F 1$s$ states on the etched As$_2$S$_3$ film surface. Samples were analyzed using an EscaLab 220-IXL under a vacuum of $\sim 10^{-10}$ torr. A monochromatic Al K$_\alpha$ x-ray source ($h\nu=1486.6$ eV) with power of 250 W was used for the analysis. High resolution spectra of C 1$s$ and F 1$s$ were obtained with a pass energy of 20 eV, 0.05 eV steps, and sweep numbers from 5 to 10, depending on the intensity of the peak. C–C bonding was selected as the internal reference and the binding energy of C 1$s$ line was referenced as 285.0 eV.

### III. RESULTS

The etching of As$_2$S$_3$ using CF$_4$–O$_2$ plasma had several drawbacks, such as a large etch bias; a nonvertical edge profile; and rough etched surfaces. These originate from the high PR ER and the strong chemical etching nature due to the abundant fluorine radicals in the plasma. A CHF$_3$ plasma is known to have lower F-atom and higher CF$_3$ radical densities compared to CF$_4$ and CF$_4$–O$_2$. This enables, for example, selective dry etching of SiO$_2$ against Si aided by enhanced fluorocarbon polymer deposition. Moreover, the polymer deposited on the etched sidewall prevents lateral erosion of the patterns and, as a result, vertical profiles can be obtained. Thus, we tried to utilize the higher polymerization tendency of CHF$_3$ plasma to achieve both an improvement in the etch selectivity and vertical sidewalls for micron-sized As$_2$S$_3$ waveguides.

The DOE approach is a structured, organized method for determining the relationship between factors (Xs) affecting a process and the output of that process (Y). In our study this technique was employed to investigate the etch characteristics in response to variations in the process parameters. We experimented using a two-level, half-factorial design with four factors and a center point. The lower and upper levels of the bias power, induction power, pressure, and gas flow rate were 20/40 W, 200/400 W, 5/15 mTorr, and 10/30 SCCM (SCCM denotes cubic centimeter per minute at STP), respectively. The ER of As$_2$S$_3$ and the etch selectivity for each sample are tabulated with the plasma etching conditions in Table I. Figure 1 shows the main effect plots for the ER of As$_2$S$_3$ and PR, and their ratio, i.e., the etch selectivities, as a function of these four parameters. These plots show the average change in the output when a factor is changed from its low level to its high level. From this the importance of each factor in determining the output can be deduced. As shown in the figure the ER of As$_2$S$_3$ increases sharply with induction power and with the inverse of the flow rate, but is nearly

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bias power (W)</th>
<th>Induction power (W)</th>
<th>CHF$_3$ flow rate (SCCM)</th>
<th>Gas pressure (mTorr)</th>
<th>Etch rate of As$_2$S$_3$ (nm/min)</th>
<th>Etch selectivity</th>
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<td>i</td>
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**TABLE I. Plasma etching conditions, the etch rate of As$_2$S$_3$, and the etch selectivity for each sample.**

![FIG. 1. (Color online) Main effect plots (data mean) for the etch rate of As$_2$S$_3$ and PR, their ratio (selectivity) as a function of bias power (RF1), induction power (RF2), pressure (p), and flow rate (FR). The datum point in the lower or upper level denotes the mean of four data points, while blue dots at the center represent a single value.](image)
independent of the bias power and pressure. On the other hand, the ER of the PR has a strong correlation with the bias and induction power, while it is almost independent of the pressure and flow rate. As a result, the etch selectivity of As$_2$S$_3$ against PR decreases with bias power and flow rate. The observed etch rate of As$_2$S$_3$ ($\sim$300–800 nm/min) is quite suitable for waveguide fabrication. For example considering a 1 $\mu$m etch depth, the process time is neither too long nor too short to compromise accurate control of the etch depth. Furthermore, the observed etch selectivity in CHF$_3$ plasma was improved so significantly compared to CF$_4$–O$_2$ plasma that any condition within the investigated domain could be employed for processing the waveguides.

The effect of the process parameters on the etched profile and surface roughness is also evident from the cross-sectional SEM images of the patterned waveguides (Fig. 2). The profiles ranged from isotropic to negative or positive sloped. The sidewall shapes were significantly affected by the induction power and the CHF$_3$ flow rate, which are also the main factors that determine the etch rate of As$_2$S$_3$. Isotropic profiles were observed at high induction power and low flow rates (samples v and vi) coinciding with the highest As$_2$S$_3$ etch rates. On the other hand positively sloped sidewalls were found in some samples (iii, iv, and viii), which corresponded to low etch rate and/or etch selectivity. In all cases except those of samples iv and vii, the etched As$_2$S$_3$ surfaces were smooth. At high flow rate and pressure, the surface appears to be covered by polymer micromasks. Moreover, the masks are so dense on the surface of the sample iv that the etching of the film almost stopped.

Interestingly, the sidewalls of the waveguides that had vertical etched profiles were smoother than those obtained in conditions that led to the isotropic etching. Figures 3(a) and 3(b) are SEM images showing the morphologies of As$_2$S$_3$ waveguide sidewalls when the etched profile was isotropic (sample vi) and vertical (ix), respectively. This is important because smooth etched sidewalls are essential for compact optical waveguides to minimize surface scattering loss.

To further understand the mechanisms behind the profile evolutions we investigated the effect of CHF$_3$ flow rate on the etched sidewall and the surface roughness. A series of cross-sectional SEM images in Fig. 4 shows the profile changes as the CHF$_3$ flow rate is changed over values of 3, 7, 10, 20, 30, and 50 SCCM. In this study the other parameters were fixed at 10 mTorr of pressure; and 30 and 300 W of bias and induction power, respectively. It is clear that the profiles evolved from isotropic to positively sloped with increasing flow rate and also that micromasks start to appear at the higher flow rates. Furthermore, a smooth etched sidewall was observed when the sidewall was vertical [Fig. 4(d)] while it appeared to be grainy when the profile was isotropic [Fig. 4(c)].

XPS was performed to study polymer deposition on the etched As$_2$S$_3$ surface as a function of the CHF$_3$ flow rate. This method is very surface sensitive; most of the signal coming from a region extending only $\sim$2 nm below the surface. The spectra of C 1$s$ and F 1$s$ in Fig. 5 were taken from the As$_2$S$_3$ surface after 1 $\mu$m deep etching. The CHF$_3$ flow rates were 10, 20, 30, and 50 SCCM while the bias power, induction power, and pressure were fixed at 30, 300 W, and 10 mTorr, respectively. The chemical origins of the different peaks are indicated in the graphs. The C 1$s$ spectrum obtained at 10 SCCM has the same position and shape of that obtained from an as-deposited As$_2$S$_3$ film surface and is likely originate from carbon contamination from air exposure before it was loaded into the XPS chamber. The sample surface did not, however, contain any F, as shown in Fig. 5(b). As the flow rate was increased, the C 1$s$ spectrum broadens, especially on the higher binding energy side and at the same time the F 1$s$ spectrum grows. Several subpeaks originating from CF$_x$ ($x=1,2,3$) polymer are discernible in the C 1$s$ spectrum when the CHF$_3$ flow rate was 50 SCCM. Note that the etched surface was covered heavily with polymer micromasks in this etching condition [refer to Fig. 4(f)].
the intensities at 282 and 692 eV, respectively.

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mTorr, respectively. The C 1s directionality due to the bias power plays a decisive role in densities of F-atoms, CF radicals, or ions that perform the deposition or etching processes. Hence, CHF3 plasma is a mixture of electrons, radicals (e.g., F, CFx), ions (e.g., CFx+), and CHF3 molecules. Fluorine atoms in the plasma react spontaneously with As2S3 at ambient temperature and form volatile compounds, such as AsF3 and SF6\(^{10}\). CFx (x=1, 2, 3) radicals, particularly CF2, are expected to be the main passivation precursors in fluorocarbon plasmas.\(^{11}\) Even though the number of ions is very small (a few ppm) relative to the neutral species in the plasma,\(^{12}\) their directionality due to the bias power plays a decisive role in obtaining a vertically etched profile.

Each species is not only generated by electron-impact dissociation and ionization but also disappears by recombination with other species, consumed in the etch reaction, or pumped out of the reactor. Therefore, the observed etching characteristics, such as the etch rates, the etch selectivity, and the edge profile can be understood in terms of the relative densities of F-atoms, CFx radicals, and ions in the plasma which are themselves determined by the process parameters.

In an ideal reactor the bias power relates to the ion acceleration and bombardment energy but not the density of the particular species. On the other hand the induction power determines the generation rate of radicals and ions. An increase in gas pressure normally leads to an increase in the radical density but a decrease in the ion density. Furthermore, an increase in the gas pressure reduces the mean free path before collisions so that the ion energy drops. The residence time (\(\tau\)) of the gas, i.e., the mean time it remains in the process chamber before being pumped away, is determined by the gas flow rate at constant pressure and is expressed by

\[ \tau = \frac{V}{S} = \frac{PV}{Q}, \]

where \(V\), \(S\), \(P\), and \(Q\) are the volume of the reactor, exhaust rate, pressure, and flow rate, respectively. High gas flow (i.e., short \(\tau\)) at constant pressure means high pumping speed. This results in more rapid loss of neutral species having longer lifetime which might enhance ionization; hence a large number of radicals can be generated due to the reduced recombination of them and small ion density.\(^{13}\)

We can deduce the etch mechanisms of a particular material from its etch rate dependence on the process parameters. For instance the etch rate of the PR in Fig. 1 increases with bias and induction power, but is almost independent of the CHF3 pressure and flow rate. Therefore, ion attack on the PR, that is proportional to the ion energy and density, cannot fully account for the PR etching mechanism because the ion energy and density in the plasma normally increase with bias and induction power, but decrease with the pressure and flow rate. It is known that F-radical can also attack PR by abstraction of hydrogen from organic polymers.\(^{14}\) Additionally, the density of F-atoms increases with the induction power, pressure, and flow rate. Consequently, it can be concluded that PR is etched not only by ion bombardment but also through a reaction with the fluorine radicals.

Similarly it is evident that chemical reactions with fluorine radicals is the dominant As2S3 etching mechanism.\(^{1} \) This can again be deduced from the etch rate dependence of the process parameters, namely, the rate increases with induction power and with the inverse of the flow rate, but changes little with the pressure or bias power. Moreover, the fact that the substrate temperature had little influence on the etch rate indicates the activation energy for the reaction—As2S3 with F-atoms to form volatile compounds—is quite small. These features are very similar to the etching of silicon in fluorine-containing plasma.\(^{15}\)

It is worthwhile noting that the gas flow rate affects all the observed etching characteristics significantly, especially the etched profile and the surface roughness which are crucial parameters for compact optical waveguides. Therefore, we need an in-depth understanding of the role of the flow rate and its correlation with other process parameters. Only a few reports have dealt with this issue, and therefore it is useful to construct an model to explain the plasma etching behavior of As2S3 films. Our model is based on the notion that the relative densities of F-atoms, CFx, and ions determine the etch rates, the etch selectivity, the edge profile, and the etched surface roughness.

As the gas flow rate increases (i.e., the gas residence time gets shorter), the CFx and F radical densities increase while the ion density decreases.\(^{13}\) Since ion bombardment contributes little to the removal of the polymer film on the As2S3 surface at reduced ion density, the [F]/[CFx] ratio decreases.
should be an indicator of the following. A low \([F]/[CF_x]\) ratio will lead to increasing polymer deposition on the film surface and this will slow down the etch rate. At a higher \([F]/[CF_x]\) ratio, however, the etching reaction should not be impeded because the recombination process between \(CF_x\) and \(F\) to make \(CF_{x+1}\) decreases the polymer precursor density. In the case of \(CF_4\) plasma, \(F\)-atoms are so abundant compared to \(CF_x\) that the etch rate of \(As_2S_3\) or Si increases with the flow rate (corresponding to and increase in \([F]\)) tending to saturate at the highest rates. However, the \(F\) density in \(CF_3\) is known to be only \(\approx 10\%\) of that in \(CF_4\) due to the scavenging action of the \(H\) atoms. This is the reason the \(As_2S_3\) etch rate decreases with increasing flow, even in relatively small flow regime. (Refer to Fig. 1.)

The \(CHF_3\) gas flow also dramatically influenced the etched profiles as well as micromask formation, as shown in Fig. 4. Those changes can also be explained in the same way, i.e., via the relative densities of the three species—\(F\), \(CF_x\), and ions. Note that ion motion induced by the bias power is directional while the polymer deposition is isotropic. At small flows (i.e., long residence time) it is difficult for polymer to form on the etched surface due to the reduced precursors density. Moreover, the relatively high ion numbers and energy can remove the polymer easily from the surface. Hence, the chemical reaction with \(F\)-atoms makes the etching of the edge isotropic. The opposite is the case at high flow rate. Polymer deposition prevails over ion bombardment so that a protective layer covers the surface even that in the plane of the film. In these conditions, the profile becomes positively sloped because the deposited polymer layer becomes thicker as the etching proceeds. Incomplete removal of the polymer layer on the plane surface results in the formation of polymer micromasks [see Fig. 4(f)]. The irregularity of the etched surface caused by the micromasks is undesirable in rib-type waveguide because it results an increase in the optical scattering loss.

It is possible to identify optimal process conditions in terms of the etch profile and minimal micromasking and this occurs at moderate flow rates [see Fig. 4(d)]. Under these conditions there seems to exist the right balance between spontaneous chemical etching, deposition of the passivating species to protect the sidewall, and ion bombardment to remove the passivating layer at the bottom of the pattern to allow etching to continue. As shown in Fig. 3, polymer passivation has an added benefit, namely, in the best etching conditions it results in a smooth etched sidewall. When the polymer deposition is insufficient, isotropic chemical etching occurs by the \(F\)-atoms on the unprotected sidewall and this results in a large etch bias and also makes the etched surface grainy due to the inherent nanoscale phase separation of \(As_2S_3\) film.

The XPS study on the etched films strongly supports this interpretation. Figure 5 clearly shows the content of fluorine, the main element in the polymer, increases on the etched surfaces with the flow. In addition, the polymer micromasks observed at high flow rate correlate with subpeaks in the high binding energy side of C 1s originating from \(CF_x\) (\(x = 1, 2, 3\)) polymer. The ratio of \(F\) and \(C\) reduces with the inverse of gas flow due to the enhanced ion density, just as the ratio decreases with ion bombardment or bias power.

So far we have discussed the effect of the \(CHF_3\) flow rate on the etch characteristics, without considering its interaction with other parameters. If we examine Fig. 2 closely, we can see that the other parameters also play a role. For example, the edge profiles were altered when the films were etched at the same flow rate (10 SCCM) but at different induction powers—the profile being isotropic at 200 W but almost vertical at 400 W (see i, ii, iv, and v in Fig. 2). This can be explained by the increase in \([F]/[CF_x]\) ratio with induction power. Additionally, comparing the four samples etched at high flow, we can observe that the gas pressure and bias power also influence the etch behavior. High pressure enhances the polymer deposition so that the micromasks form very densely on the surface, and this result in etching of the film terminating (compare iii and iv in Fig. 2). On the other hand the enhanced ion action at low pressure or high bias power effectively removes the micromasks (see iii and vi in Fig. 2).

V. CONCLUSION

We have investigated the process parameters for patterning \(As_2S_3\) waveguides using \(CHF_3\) plasma. Enhanced polymer deposition results in good etch selectivity over PR; vertically profiled patterns; and small etch bias which are all required in order to produce compact waveguides. Furthermore, smooth etched sidewalls found for waveguides which had vertical sidewalls—this being important to reduce the optical scattering loss. We identified the process conditions that led to the optimal relative densities of \(F\)-atoms, \(CF_x\), and ions in the plasma. We conclude that \(CHF_3\) is a good choice for plasma processing of \(As_2S_3\) film. This was demonstrated recently by the improved optical performance of waveguides fabricated using this process.

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