Nanoscale phase separation in ultrafast pulsed laser deposited arsenic trisulfide (As_2S_3) films and its effect on plasma etching

Duk-Yong Choi,^{a)} Steve Madden, Andrei Rode, Rongping Wang, and Barry Luther-Davies
Centre for Ultrahigh Bandwidth Devices for Optical Systems, Laser Physics Centre, Research School of Physical Science and Engineering, The Australian National University, Canberra 0200, Australia

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We have observed nanoscale phase separation in amorphous arsenic trisulfide (As_2S_3) films produced by ultrafast pulsed laser deposition and its effect on the surface morphology of the film after plasma etching. When the film was etched in $\text{CF}_4\text{--O}_2$ plasma, a grainy structure was observed on the surface. From Raman and x-ray photoelectron spectroscopies, we concluded that the grainy structure of the etched surfaces comes from the differential chemical attack between different phases in the film. © 2007 American Institute of Physics. [DOI: [10.1063/1.2798936](https://doi.org/10.1063/1.2798936)]

I. INTRODUCTION

Chalcogenide glasses (ChG) contain the chalcogen elements (sulfur, selenium, or tellurium) as a substantial constituent covalently bonded to network forming elements such as Ge, As, Sb, and Si. Although already widely used as phase change materials for optical data storage and nonvolatile random access memories, ChGs are also good candidates for integrated all-optical devices due to their high third order optical nonlinearity and low linear and nonlinear optical losses.¹ Laser writing has earlier been used to produce chalcogenide waveguides by utilizing the well-known photosensitivity of these materials to light near their band edge. The photoinduced refractive index change is, however, generally not stable due to the relaxation of the glass structure, which makes this approach unsuitable for practical devices. We have, therefore, adopted the use of plasma etching to fabricate As_2S_3 rib waveguides.²

Typically, the third order optical nonlinearity (n_2) of chalcogenide glasses is in the range 100–1000 times that of fused silica. In order to reduce the operating power of all-optical devices used for functions such as optical regeneration,³ wavelength conversion,⁴ or demultiplexing,⁵ the nonlinear parameter $\gamma (=n_2\omega_0/A_{\text{eff}}$, where A_{eff} is the effective mode area of the waveguide and ω_0 the angular frequency of the propagating wave) should be high, while the propagation length in the waveguide should be as large as practical. This means that the waveguides must have a very small cross section ($<\text{few } \mu\text{m}^2$) and a high refractive index contrast between the core and cladding to confine the optical field in the structure to minimize A_{eff} as well as low propagation losses. Dry etching is the natural choice for fabricating such structures and offers the benefits of tight dimension control, vertical profile, and clean process compared with wet etching reported by other researchers.^{1,6,7} As A_{eff} drops, however, it is well known that structural imperfections particularly surface roughness induced by device fabrication

process—film deposition, lithography, and etching—becomes the dominant source of optical loss.⁸

In this work, we investigated the grainy morphology due to the intrinsic nanoscale phase separation characteristic of As_2S_3 films that appears after plasma etching. This is an additional source of surface roughness and could degrade the optical performance of a device. We have found that a grainy surface was produced when the film was etched chemically in $\text{CF}_4\text{--O}_2$ plasma. On the other hand, argon sputter-etched films did not show any morphological change compared to as-deposited film surface. Although Raman spectroscopy indicated that several phases or clusters exist in the as-deposited films, it did not give information on the size of each phase and the way they are distributed in the film. Therefore, we performed surface-sensitive x-ray photoelectron spectroscopy (XPS) and found that the content of As–As and S–S homopolar bonds, which are characteristics of molecular species, such as As_4S_4 , As_4S_3 , S_8 ring, etc., differ significantly on as-deposited and $\text{CF}_4\text{--O}_2$ plasma etched films. These investigations strongly suggest that the grainy structure of the etched surface comes from the differential chemical etch rate between different phases present in the films.

II. EXPERIMENT

Commercial As_2S_3 glass (Amorphous Materials of Garland, Texas) was used as an ablation target. 2.5 μm thick As_2S_3 films were deposited on thermally oxidized silicon wafers by ultrafast pulsed laser deposition (UFPLD).⁹ This technique employs a frequency doubled mode-locked Nd:YVO₄ laser producing $\sim 25\text{--}28$ W average power (900–1000 nJ/pulse, 12 ps pulse width) at 532 nm and a repetition rate of 28 MHz. The laser beam was directed into the vacuum chamber pumped down to $\sim (3\text{--}5) \times 10^{-7}$ Torr and focused on a target with a telecentric scanning lens, providing laser peak intensity up to 2.7×10^9 W/cm² on the target surface. The vapor was deposited on the wafers placed on a rotating carousel located ~ 400 mm from the target. We verified from EDX measurement that the composition of the deposited film was the same (within ± 1 at. %) to that of target $\text{As}_{40}\text{S}_{60}$ glass. Dry etching of as-deposited film was car-

^{a)} Author to whom correspondence should be addressed. Tel.: +61-2-6125-9279. FAX: +61-2-6125-0029. Electronic mail: dyc111@rsphymail.anu.edu.au

TABLE I. XPS data fitting parameters: Δ is the doublet binding energy separation for d or p orbits, DR is the area ratio for the doublets, FWHM is the full width at half maximum of the peaks, and Mix is the Gaussian/Lorentzian mix factor of the peaks.

	Δ (eV)	DR	FWHM (eV)	Mix
As 3d	0.694	0.71	0.87	0.93
S 2p	1.185	0.505	0.9	0.91

ried out in an inductively coupled plasma reactive ion etching system (Oxford, Plasmalab-100). The processing gases (CF_4 , O_2 , and Ar) were introduced into the vacuum chamber through separate mass flow controllers.

The surface morphologies of as-deposited and plasma-etched films were investigated by atomic force microscopy (AFM) (Multimode SPM from Digital Instruments with Nanoscope IIIa Controller). We used a micromachined silicon tip with radius below 10 nm in the tapping mode because the As_2S_3 film is relatively soft. The lateral step size was 2 nm over a $1 \times 1 \mu\text{m}^2$ scan area and the height resolution was below 0.1 nm. The bond structure of the As_2S_3 glass target and the as-deposited film was probed by Raman scattering. All spectra were measured in a backscattering geometry at room temperature using a micro-Raman spectrometer (Renishaw 2000 Raman microscope). To minimize the photoinduced structural changes during the measurement, samples were excited with 782 nm light at an intensity below $1 \text{ W}/\text{cm}^2$ on the surface and each spectrum was recorded within 60 s. The resolution of the Raman spectra was 1 cm^{-1} .

X-ray photoelectron spectroscopy (XPS), which is known to be a useful method to obtain information on the local environment of an element, was applied to study the bond structure of the As_2S_3 film. This method is very surface sensitive, most of the signal coming from a region extending only $\sim 2 \text{ nm}$ below the surface. For surface analysis, the samples were analyzed using an EscaLab 220-IXL in a vacuum of $\sim 10^{-10}$ Torr. A monochromatic $\text{Al K}\alpha$ x-ray source ($h\nu = 1486.6 \text{ eV}$) at a power of 250 W was used for the analysis, while a low-energy electron flood gun was used for charge compensation. Individual high resolution spectra (As 3d and S 2p) were recorded 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. Carbon was selected as the

internal reference and the binding energy (BE) of C 1s line was referenced at 285.0 eV. The experimentally obtained binding energies of the As and S were corrected accordingly based on the C 1s reference.

For the deconvolution of each high resolution peak to their constituent subpeaks, we used XPSPEAK, the XPS data analysis software developed by Kwok.¹⁰ The Shirley baseline was used for background removal, and the subpeaks were assumed to have Voigt line shapes. Subsequently, the As 3d and S 2p peaks were deconvolved into two-parameter Voigtian peaks, using the parameters in Table I, where Δ is the doublet separation for d or p orbits, DR is the area ratio for the doublets, such as As $3d_{5/2}/\text{As } 3d_{3/2}$ or S $2p_{3/2}/\text{S } 2p_{1/2}$, FWHM is the full width at half maximum of the peaks, and Mix is the Gaussian/Lorentzian mix factor of the peak. These parameters were chosen by using pure elemental data as references and fitting optimization. The spectra were fitted with as few subpeaks as possible until the χ^2 value, which measures the goodness of the fit, reached a minimum (normally below 1). Through self-consistency of all fitting results and our understanding of the material, we assigned the peaks to different chemical environments.

III. RESULTS AND DISCUSSION

A. Plasma etching and surface morphology of As_2S_3 film

As-deposited As_2S_3 films were etched in plasma composed of a 10 SCCM (SCCM denotes cubic centimeter per minute at STP) CF_4 and 20 SCCM O_2 mixture. The chamber pressure, bias, and induction power were 10 mTorr, 20 W, and 200 W, respectively. The etch rate of the film was $\sim 1 \mu\text{m}/\text{min}$ and the etch depth was $1 \mu\text{m}$. In this plasma condition, As_2S_3 is known to be removed dominantly by chemical reactions with fluorine radicals.² For comparison, an argon plasma was applied to physically etch the film. The etching was performed in Ar flow rate of 30 SCCM, a chamber pressure of 5 mTorr, and 100 and 500 W of bias and induction power, respectively. The etch rate of As_2S_3 film was 422 nm/min in this condition and we also etched down $1 \mu\text{m}$.

Figure 1 shows the AFM images of (a) the as-deposited UFPLD film, (b) the same film etched in Ar plasma, and (c) the film etched in $\text{CF}_4\text{-O}_2$ plasma, respectively. A very

FIG. 1. (Color online) The surface AFM images of (a) the as-deposited UFPLD film, (b) the UFPLD film etched in argon plasma, and (c) the film etched in $\text{CF}_4\text{-O}_2$ plasma in $1 \times 1 \mu\text{m}^2$. The measured root-mean-square roughness (R_q) in (a), (b), and (c) are 0.3, 0.5, and 3 nm, respectively. The height scales are the same in all images (20 nm/division).

FIG. 2. Raman spectra of UFPLD as-deposited As_2S_3 film (solid line) and bulk glass target (dotted line). The intensities were normalized to the intensity of 345 cm^{-1} band.

rough and grainy structure with grain size of 30–80 nm and height up to 30 nm was observed for the film etched in $\text{CF}_4\text{--O}_2$ plasma. By comparison, the surface of the as-deposited film and the film etched in Ar plasma were relatively smooth and featureless. The measured root-mean-square roughness (R_q) for the films in Figs. 1(a)–1(c) were 0.3, 0.5, and 3 nm, respectively. We noted that a grainy surface occurred even when the sample was placed upside down so that it was not directly exposed to the $\text{CF}_4\text{--O}_2$ plasma. This ruled out the influence of any micromasking effects¹¹ as the source of the roughness. Furthermore, the surface of bulk glass As_2S_3 sample, which is much more homogeneous than the film (as is clear from the Raman spectra of two samples presented later), was not roughened by the $\text{CF}_4\text{--O}_2$ plasma etching. Consequently, it can be deduced that the extent of phase separation in the film and its chemical etching by the F radicals abundant in $\text{CF}_4\text{--O}_2$ plasmas² are responsible for the production of the grainy surface.

B. Raman spectroscopy of as-deposited As_2S_3 film and bulk glass

We further elucidated the structural properties of the as-deposited films using Raman spectroscopy. A number of papers^{12–21} have already described the microstructure of As_2S_3 films based on analyses of Raman scattering spectra; however, most of those studies were carried out on thermally evaporated films. Figure 2 shows the Raman spectra taken from an UFPLD film (solid line) and glass target (dotted line). The intensities of two spectra were normalized to those of 345 cm^{-1} bands, and the characteristic peak positions are indicated by the arrows. Two broad peaks can be observed in the $\text{As}_{40}\text{S}_{60}$ glass target. A large peak centered at 345 cm^{-1} comes from the $\text{AsS}_{3/2}$ pyramidal network, which mainly comprises the glass backbone structure.¹³ The small band at $180\text{--}250\text{ cm}^{-1}$ is related to structures containing As–As bonds, e.g., As_4S_4 molecules, which also exists in bulk glass when $x > 38\text{ at. \%}$ in $\text{As}_x\text{S}_{1-x}$.¹⁴ Thus, As_2S_3 bulk glass mainly comprises of $\text{AsS}_{3/2}$ pyramidal network and a tiny amount of an As–As bond containing phase.

The Raman spectrum taken from UFPLD film, however, shows many peaks. With reference to the literature, we can identify the peaks as follows:

- peaks at 350 and 343 cm^{-1} are associated with the orpiment (As_2S_3) phase;¹⁵
- peaks at 192 , 222 , and 360 cm^{-1} come from As–As bonds in $\beta\text{-As}_4\text{S}_4$ (realgar) monomer;^{15,16}
- peaks at 234 cm^{-1} represents As–As bonds in the glass network, such as $\text{S}_2\text{As--AsS}_2$;¹²
- weak peaks 495 cm^{-1} comes from As–S–S bond;^{12,17}
- another weak peak (denoted by *) at 275 cm^{-1} may come from the As_4S_3 phase;^{18,19}
- no As metal, which has a broad band ($170\text{--}310\text{ cm}^{-1}$) centered at 225 cm^{-1} , was observed;¹⁹
- no S_8 rings ($\sim 475\text{ cm}^{-1}$) was observed.^{17,21}

If we consider the stoichiometry of the as-deposited film, the number of S–S bonds seems to be very small compared to that of As–As bonds in the Raman spectrum. This may be due to the S–S bond-related peak at 495 cm^{-1} being obscured by the strong background from the silicon wafer ($\sim 520\text{ cm}^{-1}$). Another small peak at 275 cm^{-1} can be identified with arsenic oxide.²² However, Fourier transform infrared spectroscopy (not shown here) indicated that there was no As–O related peak in the UFPLD as-deposited film, which normally has a very strong absorption band. Additionally, we could not observe any chemical shift of As 3d from elemental to oxide forms: $\sim 3.6\text{ eV}$ for As_2O_3 and 4.4 eV for As_2O_5 in XPS measurement.²³ These Raman spectra imply that the as-deposited UFPLD film is composed of fair amounts of molecular units (As_2S_3 , As_4S_4 , and As_4S_3) as well as an $\text{AsS}_{3/2}$ glass network structure (large band at 345 cm^{-1}), and this coincides well with previous reports for thermally evaporated material.^{18,19}

Raman spectra, however, do not give quantitative information of each phase and the way in which these phases are distributed in the film and glass. Because the microstructure in chalcogenide glasses can be altered during exposure to intense electron beams,²⁴ attempts to directly observe each phase in the film by transmission electron microscope have not been successful so far.

C. XPS analysis of as-deposited and etched As_2S_3 films

The observations reported above suggest that nanoscale phase separation in these As_2S_3 films is the source of the grainy structure, which is decorated by the differential chemical attack during plasma etching. The Raman spectra confirmed the existence of several phases in the film. To strengthen this picture, we have analyzed the bond structure of As and S atoms on the as-deposited and $\text{CF}_4\text{--O}_2$ plasma-etched film surfaces. The XPS raw data and their deconvolution results are shown in Fig. 3. Due to the spin-orbit splitting, both As 3d and S 2p spectra are composed of doublets corresponding to As $3d_{5/2}$ and As $3d_{3/2}$ and S $2p_{3/2}$ and S $2p_{1/2}$, respectively. The goodness of fit (χ^2) improved significantly when the measured As 3d was fitted with two sub-peaks, 1-1' and 2-2'; here, 1 and 2 denote As $3d_{5/2}$ spin

FIG. 3. (Color online) XPS spectra for As 3d and S 2p peaks on the as-deposited film [upper two spectra (a) and (c)] and the film etched in $\text{CF}_4\text{-O}_2$ [(b) and (d)]. Due to the spin-orbit splitting, *d* and *p* orbitals comprise of doublets. 1 and 2 denote As $3d_{5/2}$ and the numbers with “'” (their doublets) denote As $3d_{3/2}$. The same for 3,4 (S $2p_{3/2}$) and 3',4' (S $2p_{1/2}$).

states and 1' and 2' denote As $3d_{3/2}$. Therefore, the As 3d spectra were deconvolved assuming two pairs of subpeaks representing two distinguishable arsenic bond configurations. The case was the same to S 2p spectrum; it could be fitted with two different bonding states, 3-3' and 4-4'. The same notation is used for 3,4 (S $2p_{3/2}$) and 3',4' (S $2p_{1/2}$). By referring the literature on BEs and chemical shifts,^{21,25} we can assign two subpeaks in As 3d for As atoms within $\text{AsS}_{3/2}$ pyramidal units at higher BE and As atoms within units containing As-As homopolar bonds at lower BE. Because arsenic has a smaller electronegativity than sulfur,²¹ homopolar As-As bond containing units contribute the lower binding energy peak. In the same manner, the S 2p orbital results show peak 3-3' as one S atom bonded to two As atoms and 4-4' as S bonded to one As and one S (i.e., homopolar S-S bonds).

From the data, we could deduce that the content of arsenic with homopolar bonds was 17% in the as-deposited film, which is quite similar to that reported for thermally evaporated films.²⁵ We found, however, that this almost doubled to 32% on the grainy etched surface. On the other hand, the fraction of S atoms containing S-S bonds decreased from 17% to 11% upon etching the as-deposited film. For comparison, we also performed XPS analysis on the As_2S_3 film surface etched with the argon plasma; however, the numbers of both As and S atoms containing homopolar bonds did not change as a result of etching. These data indicate that the grains on the etched surface are enriched with As-rich phases (e.g., As_4S_4) relative to the as-deposited film surface. In fact, the compositions of the as-deposited and etched surfaces, which were calculated from

the areas under As 3d and S 2p peaks in XPS and other parameters—sensitivity factor, transmission functions, etc.—were $\text{As}_{40}\text{S}_{60}$ and $\text{As}_{41.3}\text{S}_{58.7}$, respectively. In short, the grainy etched surface seems to be enriched with the As-rich phase, for example, As_4S_4 which is more durable than other species,²⁶ while the S-rich phase is depleted. The columnar structure reported in As_2S_3 evaporated films²⁷ might be a source of the grainy structure because grain boundaries generally have higher etch rates. However, we could not observe any columnar structure on As_2S_3 films deposited by UFPLD in high resolution cross sectional SEM.

From the XPS analysis, we can therefore conclude that the grainy surface structure characteristic of As_2S_3 films etched in $\text{CF}_4\text{-O}_2$ plasma comes from the differences in chemical etch rate between the phases which exist in as-deposited films and contain different bond configurations. The etch rate is fastest for the phase containing S-S bonds, smaller for the As-S bond, and slowest for the As-As bond.

IV. CONCLUSION

We have shown that the As_2S_3 film produced by UFPLD contains As-As and S-S homopolar bond containing phases, which are interspersed with an orpiment-type backbone network. This structural characteristic causes the rough and grainy surfaces when the film is plasma etched using $\text{CF}_4\text{-O}_2$ due to the differential chemical attack between the different phases. As a result, if this etching process is used to create an As_2S_3 waveguide, one can anticipate that waveguide sidewalls will be rough and this will enhance the optical scattering that dominates the propagation loss in high refractive index contrast waveguides. It will therefore be

necessary to adopt measures that either reduce the phase separation in the as-deposited films or the propensity for differential chemical attack. In the former case, thermal annealing or light illumination (optical annealing) can result in an increase in the orpiment backbone phase in the films, while alternative plasma chemistries may also be effective. Physical etching using Ar plasma is not a practical solution since it generally provides poor etch selectivity with the mask resulting in rib waveguides with slanted sidewalls and loss of dimensional control.

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