Dry etching of thin chalcogenide films

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Abstract. Fluorocarbon plasmas (pure and mixtures with Ar) were used to investigate the changes in the etching rate depending on the chalcogenide glasses composition and light exposure. The experiments were performed on modified commercial HZM-4 vacuum equipment in a diode electrode configuration. The surface microstructure of thin chalcogenide layers and its change after etching in CCl₂F₂ and CF₄ plasmas were studied by SEM. The dependence of the composition of As-S-Ge, As-Se and multicomponent Ge-Se-Sb-Ag-I layers on the etching rate was discussed. The selective etching of some glasses observed after light exposure opens opportunities for deep structure processing applications.

1. Introduction

Chalcogenide glasses are among the most widely known families of amorphous materials and have been extensively studied for several decades because of their many potential applications in optical imaging, optical memories and sensing elements. Most of these applications are based on the wide variety of light-induced effects exhibited by these materials [1-4]. In our previous investigations [5, 6] of the changes in the dissolution rate of thin As-S-I(Bi) we drew some conclusions connected with their practical application.

There exist experimental indications that amorphous chalcogenides have rather high non-linear optical properties and, hence, these materials are promising candidates as non-linear optical elements [7, 8].

The interest in chemical dry etching has grown considerably in recent years due to its advantages over the wet etching process. Chemical dry etching, unlike the wet stripping methods, reduces the handling and disposal of toxic chemicals and can easily be integrated into modern multi-chamber systems [9-11].

The aim of this work is to present the results of a study of the dry etching process of chalcogenide thin films depending on their composition and on the etching conditions.

2. Experimental

The bulk glasses were synthesized by direct monotemperature synthesis in vacuumed (residual pressure of 10⁻³ Pa) and sealed quartz ampoules. The As-Se glassy samples were prepared from elements of purity 5N. As initial components for the synthesis of samples of the Ge-Se-Sb-Ag-I
system we used AgI (99.99%, Merck), GeSe₂ and Sb₂Se₃ (synthesized by us from Ge, Sb and Se with purity of 5N, 4N and 5N, respectively).

Thin films of both systems were deposited by thermal evaporation in vacuum (6 - 8 × 10⁻⁶ Torr) from a Mo crucible on soda-lime and graphite substrates at room temperature. The deposition rate of 5 nm/s was monitored by a quartz thickness and deposition rate monitor (MIKI, Hungary). The thin films thickness was about 800 nm, as measured by a Talystep profilometer (Taylor-Hopson, England). The thin films were illuminated by a halogen lamp (20 mW.cm⁻²) for two hours.

The dry etching was carried out in a modified commercial vacuum installation HZM-4 (Germany). The diode electrode configuration was connected to a 2.5 MHz rf power supply. The samples were placed on the water-cooled rf electrode with a diameter of 200 mm. The rf power density was varied in the range 50 - 350 mW.cm⁻². Most of the experiments were performed at a pressure of 8 - 10 Pa and a power density of 130 mW.cm⁻². The SEM studies were carried out on a Philips scanning electron microscope.

3. Results

The composition of the bulk glasses, as well as of the thin films deposited on graphite substrates, was determined by scanning electron microscopy by an X-ray microanalyser (Joel Superprobe 733, Japan) – table 1. The results show that the elemental composition of the As-containing films is very close (within ±1 at.%) to that of the bulk samples, while the Ge-containing samples show a difference between the thin films and bulk samples content.

| Composition of bulk samples (at.%) | Composition of thin films (at.%) | CCl₂F₂ | CF₄ |
|-----------------------------------|---------------------------------|--------|-----|
| CCl₂F₂                            | CF₄                             | Unexp  | Exp | Unexp | Exp |
| As₂₈Se₇₂                          | As₂₉Se₇₃                        | 31     | 17  | 20    | 10  |
| As₄₀Se₆₀                          | As₄₁Se₅₉                        | 35     | 27  | 25    | 28  |
| As₄₅Se₅₅                          | As₄₆Se₅₄                        | 61     | 32  | 23    | 32  |
| As₄₀S₆₀                           | As₄₁S₅₉                         | 33     | 8   | 33    | 22  |
| As₃₀Ge₁₀S₆₀                       | As₃₂Ge₁₀S₅₈                     | 65     | 18  | 20    | 5   |
| As₃₀Ge₁₀S₆₀                       | As₃₂Ge₁₀S₅₈                     | 52     | 18  | 16    | 8   |
| As₁₀Ge₃₀S₆₀                       | As₁₁Ge₃₃S₅₆                     | 25     | 16  | 13    | 18  |
| Ge₄₀Se₆₀                          | Ge₄₂S₅₈                         | 9      | 18  | 21    | 5   |
| Ge₃₃Se₅₇                          | Ge₃₁Se₆₉                        | 3.3    | -   | 7.2   | -   |
| Sb₄₀Se₆₀                          | Sb₄₁Se₅₇                        | 1.6    | -   | 0     | -   |
| Ge₁₀Se₄₄Sb₁₇                      | Ge₁₄Se₄₆Sb₂₆                    | 5      | -   | 55    | -   |
| Ge₂₀Se₅₇Ag₁₇                      | Ge₂₃Se₆₂Ag₁₇                    | 4.1    | -   | 5     | -   |
| Ge₁₇Sb₁₆Ag₁₆                      | Ge₁₇Sb₁₂Ag₁₈                    | 6.7    | -   | 45.8  | -   |

Table 1. Data for the elemental composition of bulk samples and thin films. Dry etching of unexposed and exposed (800 nm) thin chalcogenide films in CCl₂F₂ and CF₄ plasmas: pressure 8 - 10 Pa; rf power density 130 mW/cm²; etching time 120 s; gas flow 15 ccm/min.

In our previous paper [12] we showed that the optimal conditions for dry etching of chalcogenide thin films are pressure of 8-10 Pa; rf power density of 130 mW/cm²; gas flow of 15 ccm/min. The changes in the etching rate depending on the film composition and exposure to light for a wide range of film compositions were studied. We did not find any difference in the etching rate of As-containing chalcogenide films using a mixture of Ar and Freon gases. We showed experimentally that the etching rate of all chalcogenide films decreases when the etching time increases. This is why in this study we compared the etching rate after 120 s etching time. The results are shown in table 1.

It is seen that the etching rate of unexposed thin As-S-Ge films decreases as the Ge content in the films is increased. After exposure, a negative etching effect was observed after applying CCl₂F₂ or CF₄.
plasmas due to densification in their structure. The etching rate of As-Se films is higher when a CCl₂F₂ plasma is applied for etching than when CF₄ gas is used, which could be explained by the higher reactivity of the former gas. We observed that illumination causes photodarkening of As-containing films (associated with structural changes). This is the reason for the difference between the etching rate of as-deposited and exposed thin films. We also observed that the selective etching (the ratio between the etching rate of exposed to light and unexposed films) in CCl₂F₂ plasma is the highest for thin As₆₀Se₄₄ layers (negative etching process), while in CF₄ plasma for films with the same composition the etching process is positive (higher etching rate for exposed layers). The etching rate depends on the chemistry of the reactions taking place between CCl₂F₂ (CF₄) and the thin films from the As-Se (As-Ge-S) systems, as a result of which areas with different structural units (AsSe₃/₂, GeSe₄/₂, SeSe₂/₂ and SS₂/₂) are attacked and volatile (AsF₆, SeF₆, GeF₄, SF₆, SF₄ and S₂F₂) and condensed (pasivating: AsF₃, AsCl₃, AsCl₅, SeF₄, GeCl₄ and S₂F₁₀) components are produced.

For the Ge-containing samples the dry etching rate in CF₄ is much higher than that in CCl₂F₂ with the exception of composition Sb₄₃Se₅₇, which is related to the high chemical activity of the F-atoms. The “anomaly” of the films with composition Sb₄₃Se₅₇ is due to the specific features of the chemical reaction’s products formed on the etched surface – SbCl₃ and SbF₃. SbCl₃ is characterized by a lower melting temperature and a higher tendency for sublimation compared to SbF₃. The etching rate for the film with composition Ge₂₈Se₆₂Ag₃I₇ is the same in CF₄ and CCl₂F₂ plasmas since the Ag in the form of AgF and AgCl blocks the film surface.

We used scanning electron microscopy to observe how the surface microstructure changes during the etching process. We plan to continue this study by using AFM to quantify the surface topology. SEM micrographs of the surface of as-deposited, etched and etched after illumination samples are shown in figures 1-3. It is seen that the surface of unexposed thin As-Se films is smooth. It remains smooth after etching in CF₄, while when the layers are etched in CCl₂F₂ grains with size of 100-200 nm appear due to the chemical reaction on the chalcogenide layer surface. No difference between the surface microstructure of unexposed and exposed films after etching is seen.

![SEM micrographs of the surface of thin As₆₀Se₄₀: (a) as-deposited, unetched; (b) etched and (c) exposed and etched in CCl₂F₂ plasma.](image)

![SEM micrographs of the surface of thin As₄₅Se₅₅ films: (a) as-deposited, unetched; (b) etched in CF₄ and (c) etched in CCl₂F₂ plasma.](image)
Figure 3. SEM micrographs of thin as-deposited Ge-containing films etched in CCl$_2$F$_2$ plasma:
(a) GeSe$_2$, (b) Sb$_2$Se$_3$, (c) Ge$_{28}$Se$_{62}$Ag$_3$I$_7$.

4. Conclusions
We studied the dry etching process of a wide range of film compositions (binary thin As-Se, ternary
As-S-Ge and multicomponent Ge-Se-Sb-Ag-I chalcogenide films) and we showed that the etching rate
depends on their composition, etching time and light exposure. For the first time we deposited thin
layers from such complex systems and showed that we can control the film composition by changing
the evaporation conditions. The chalcogenide layers surface is very smooth; after etching, and
depending on the film composition and the etching gas, grains with different sizes appear. The light
exposure causes changes in the thin layers structure and leads to different changes in the etching rate
depending on the plasma chemical composition. Good selectivity is demonstrated for some
composition, which gives a possibility for applying such chalcogenide layers in planar optical
technologies.

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