

WET-ETCHING OF SB-SE THIN FILMS OF STOICHIOMETRIC COMPOUND AND WITH EXCESS SELENIUM

Abstract

The present paper deals with the wet etching of $\text{Sb}_x\text{Se}_{100-x}$ ($x=20, 40$) thin films. Etcher was used to investigate the changes in the etching rate depending on the chalcogenide glasses composition and light exposure. The surface microstructure of thin chalcogenide layers and its change after etching were studied by SEM and AFM. The selective etching of Sb-Se thin film observed after light exposure opens opportunities for deep structure processing applications.

Keywords: *amorphous and crystalline phases, chalcogenide thin film, etching process.*

1. Introduction

Chalcogenide glasses are very promising materials because of their unique physico-chemical properties. One of the most studied phenomena in these glasses is based on photoinduced change in physico-chemical properties on exposure to bandgap light (typically in the visible or near infrared (NIR) region of the spectrum) (Stronski 2000: 973-978, Vlcek 1994: 969 – 973).

These materials can be used in the photolithography as a high resolution registering media or inorganic photoresists. The utilization of chalcogenide thin films in gray scale lithography is based on different dissolution rates of exposed and unexposed parts of the film. The different etching rates occur as a consequence of photostructural changes induced by band- or sub-band gap energy exposure (Tanaka 2006: 2580-2584). Such media provide a resolution capability of the order of several nanometers due to their amorphous structure (Utsugi 1992: 161-163) and ability to produce surface relief after exposure and treatment.

On another hand, these materials can be used as data storage media. High-speed phase transformation from “amorphous” to “crystalline” state has been widely studied as a suitable medium both for erasable (Utsugi 1992: 161-163) and WORM (Orava 2007: 1008–1013, Orava 2008: 533-539) applications. In this context the creation of micro- and nano-scaled thin film samples becomes especially interesting and important.

Although a number of articles about selective wet-etching of amorphous/crystallized phases have been published (Gerbreder 2007: 3153-3156, Orava 2007: 1441-1445, Orava 2006: 1637-1640, Vlček 2003: 515-518), very scanty information is available in the literature on such process in $\text{Sb}_x\text{Se}_{100-x}$ thin films. That is why our attention has been attracted to in situ real-time study of chemical etching process in $\text{Sb}_x\text{Se}_{100-x}$ ($x=20, 40$) thin films.

2. Experimental

Thin film was prepared by thermal evaporation technique from bulk glass samples of composition $\text{Sb}_{20}\text{Se}_{80}$ in vacuum 10^{-5} Torr onto BK-7 glass substrates at room temperature. Film thickness was controlled during evaporation by means of interference technique, as it was shown by Sledevskis (Sledevskis 2007: 51-59). Thickness of prepared film was about 300 nm. The composition and structure of the deposited layers have been analyzed using the INCA x-act detector and X-ray diffractometer SmartLab Rigaku.

During process of formation of micro-scale structures photolithographic techniques were used to illuminate and then pattern photoresist.

Confocal laser-scanning microscope Leica TCS-SPE and scanning Electron Microscope TESCAN VEGA were used to study the modification of thin films induced by light. Leica TCS-SPE was used for in-situ study of thin film etching process.

Local optical-crystallization of Sb-Se thin films was carried out using He-Ne laser, $\lambda = 633$ nm and output energy 16mW for 30 min. Organic based solution e.g. amines was used for selective etching of optically crystallized/amorphous and thermally crystallized/amorphous thin films.

The dissolution rate was measured by interference of He-Ne laser beam ($\lambda = 633$ nm, output energy: 0.013 mW) on decreasing thickness of thin film during wet dissolution process. The dependence of thickness on etching time was calculated from interference curve and the dissolution rate v (nm/s) as the slope of the curve was read.

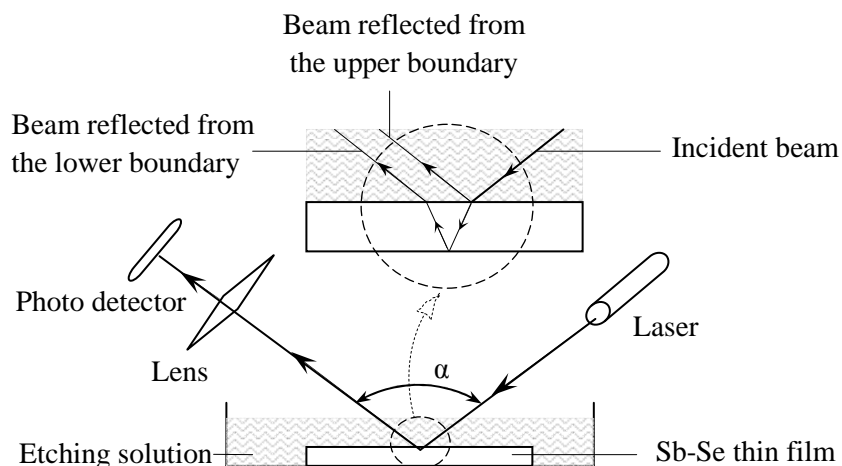


Figure 1: A schematic of the experimental wet-etching setup.
In microscope Leica TCS-SPE $\alpha=0$.

3. Results

The amorphous $\text{Sb}_{20}\text{Se}_{80}$ thin film was crystallized in the area irradiated by laser beam. Locally optically crystallized/amorphous thin films were selectively etched. The amorphous part is completely dissolved in the range of etching time 130 s for $\text{Sb}_{20}\text{Se}_{80}$ and 760 s for $\text{Sb}_{40}\text{Se}_{60}$, whilst the crystallized area could be considered as insoluble as it is schematically depicted on Fig. 2 for optically induced crystallization. With an increase in the percentage of Sb in Sb-Se compound etching rate decreases.

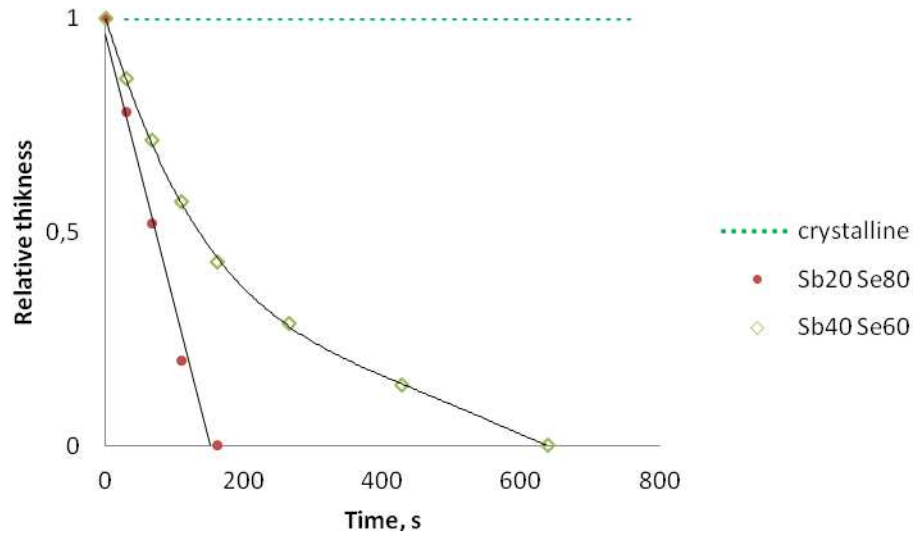


Figure 2: Kinetics of dissolution of amorphous and crystalline phases of Sb-Se in organic etcher (room temperature).

Microanalysis shows significant change in composition between amorphous, crystallized not etched and crystallized selectively etched $\text{Sb}_{20}\text{Se}_{80}$ sample. Quantitative results taken on this specimens are listed in Tables 1.

Table 1. Quantitative microanalysis with an Oxford INCA. Starting compound for evaporation is $\text{Sb}_{20}\text{Se}_{80}$

Spectrum	Sb	Se	Sample
Spectrum 1	20	80	As-deposited, amorphous
Spectrum 2	30	70	Cristallized, non-etched
Spectrum 3	40	60	Crystallized, etched

As we can see from Table 1, the percentage of antimony increases during laser irradiation. This probably occurs because of the loss of selenium through volatilization: on heating in the air SeO_2 is formed and sublimates (Jain 2009: 96-102, Small 2001: 59-69). The percentage of antimony increases during the etching process for $\text{Sb}_{20}\text{Se}_{80}$. In the case of the composition of $\text{Sb}_{40}\text{Se}_{60}$ percentage remains unchanged (Table 2).

Table 2. Quantitative microanalysis with an Oxford INCA. Starting compound for evaporation is $\text{Sb}_{40}\text{Se}_{60}$

Spectrum	Sb	Se	Sample
Spectrum 1	40	60	As-deposited, amorphous
Spectrum 2	40	60	Cristallized, non-etched
Spectrum 2	40	60	Crystallized, etched

The presence of the substantial amount of Sb–Se and Se–Se bonds in these glasses are responsible for this differences: the Se–Se bonds (bond energy 205.8 kJ/mol) will be ruptured soon by the etchant, whereas Sb–Se bonds, which have higher bond energy 214.2 kJ/mol, partially remain unruptured during the etching process (Starbov 1998: 209-214). The change of the dissolution rate between amorphous and crystalline phase for Sb–Se thin films is connected with changes of the structure upon the illumination. Results (Fig. 2) show a pronounced decrease in the etch rate with an increase the degree of cristallinity right up to zero etch rate for crystalline phase.

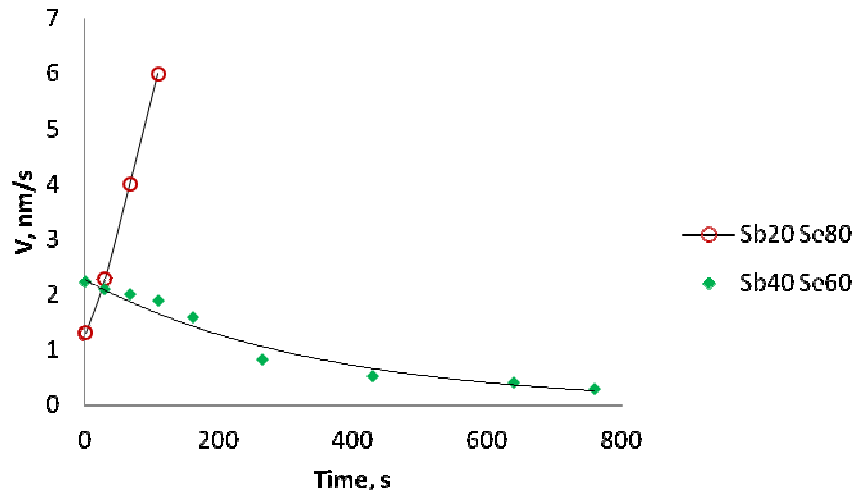


Figure 3: Time dependent etching rate during wet-etching of Sb–Se thin films.

From the above it follows that the nature of a qualitative change in the etching rate depends on the ratio of Sb–Se and Se–Se bonds in the sample. As we can see from the Figure 3, etching rate of $\text{Sb}_{20}\text{Se}_{80}$ increases with time, while the same characteristic for $\text{Sb}_{40}\text{Se}_{60}$ reduces.

Only laser crystallized spot remains after completion of the wet-etching process (Fig.

4).

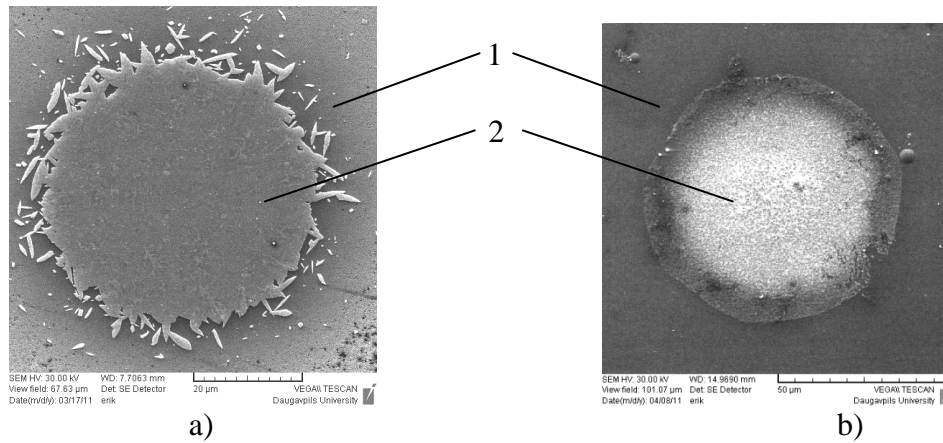


Figure 4: The SEM images of crystallized spot in $Sb_{40}Se_{60}$ (a) and $Sb_{20}Se_{80}$ (b) thin films (1 – substrate, 2 – crystalline phase).

Surface of the laser crystallized spot of $Sb_{40}Se_{60}$ is sufficiently flat and smooth, with no roughness (Fig.5). Formation of wrinkled pattern occurs due to laser irradiation of $Sb_{20}Se_{80}$ thin film (Fig.6).

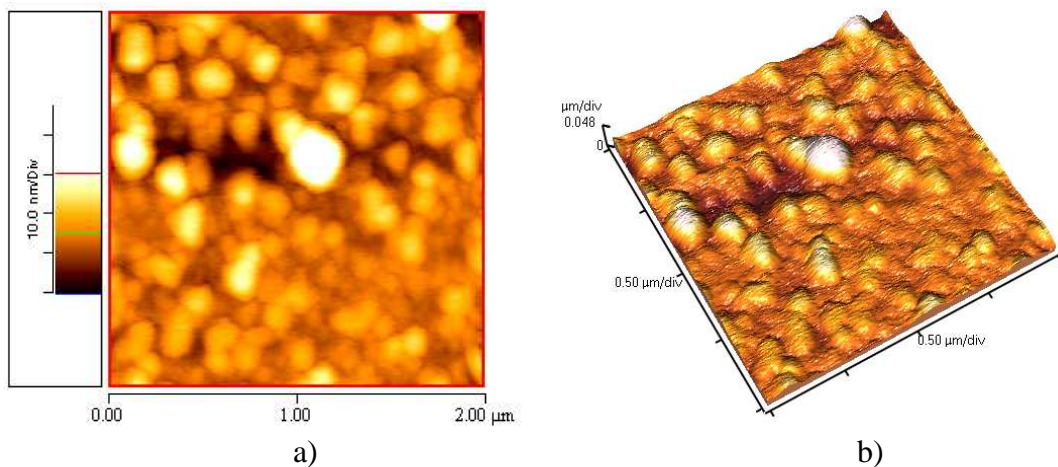


Figure 5: AFM 2d (a) and 3d (b) images for crystallized $Sb_{40}Se_{60}$ thin films.

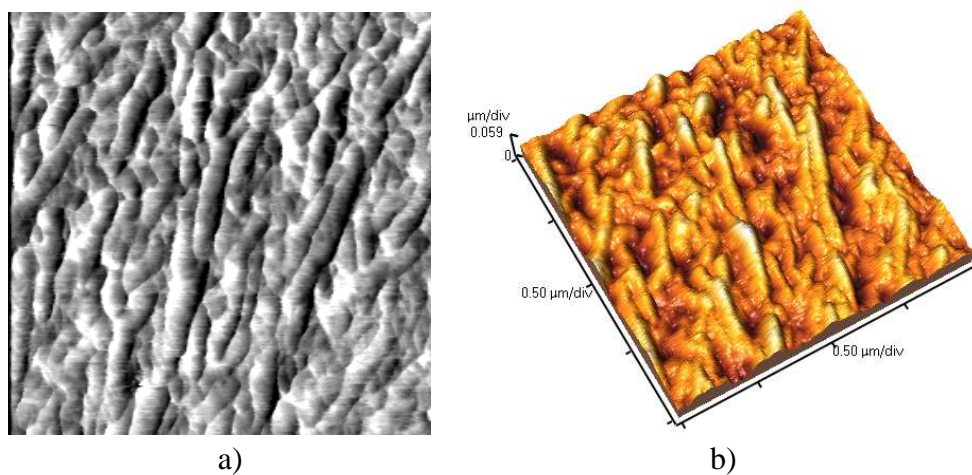


Figure 6: LFM 2d (a) and AFM 3d (b) images for crystallized $\text{Sb}_{40}\text{Se}_{60}$ thin films.

The selective etching is very effective method for microscale elements fabrication therefore the deeper study of interaction between etching solution and material should be done. The different dissolution rates between amorphous and crystalline phase would be also used to stabilize in phase change type recording applied in DVD technique and new type of memories.

Rather smooth and homogeneous surface of the samples either after the photo- and thermal stimulation or after etching process as well as fine crystalline structure makes the Sb-Se composition attractive and promising for electron-beam lithography.

Conclusions

Selective etching of Sb-Se chalcogenide thin films in organic solutions of amines was performed. Phenomenon of different etching rates in dependence of the degree of crystallization demonstrated and discussed.

The evaluation of the in-situ etching rate method was successful and this thesis proved the method would be a very useful instrument. It was even possible to measure the changes of etching rates under a dynamic etch process as done for the Sb-Se thin films.

Potential application of selective etching could be expected in the field of micro optical elements fabrication i.e. grids, waveguides, microlenses, highlighting phase change type recording memories.

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