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Selective Wet-Etching of Amorphous/Crystallized $Sb_{20}se_{80}$ Thin Films

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***Abstract*—**The selective wet-etching of amorphous and crystalline region of $Sb_{20}Se_{80}$ thin films was carried out using organic based solution e.g. amines. We report the development of an in situ real-time method to study the wet chemical etching process of thin films. Characterization of the structure and surface of films studied by X-ray diffraction, SEM and EBSD methods has been done and potential application suggested.

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

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I. Introduction

CHALCOGENIDE glasses are very promising materials because of their unique physico-chemical properties. One of the most studied phenomenon 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) [1], [2].

These materials can be used in the photolithography (izdzēsta frāze) 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 [3]. Such media provide a resolution capability of the order of several nanometers due to their amorphous structure [4] 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 [4] and WORM [5] – [6] 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 [7] – [11], very scanty information is available in the literature on such process in Sb_xSe_{100-x} thin films. That is why our attention has been attracted to in situ real-time study of chemical etching process in $Sb_{20}Se_{80}$ thin films.

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II. Experimental

Thin film was prepared by thermal evaporation technique from bulk glass samples of composition $Sb_{20}Se_{80}$ in vacuum 10^{-5} Torr onto BK-7 glass substrates at room temperature. Film thickness was controlled during evaporation by means of interference technique at wavelength of 650 nm, as it was shown in [12]. Thickness of prepared film was about 300 nm. The composition and structure of the deposed layers have been analyzed using the INCA x-act detector, EBSD system and X-ray difractometer SmartLab Rigaku.

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

The dissolution rate was measured by interference of He–Ne laser beam (λ = 633 nm, output energy: 0.013 mW) on decreasing thickness of thin film during wet dissolution process (Fig.1).

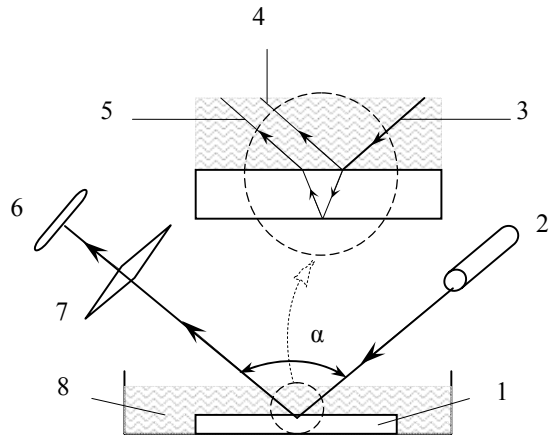


Fig. 1 A schematic of the experimental wet-etching setup. In microscope Leica TCS-SPE α=0

1, $Sb_{20}Se_{80}$ thin film; 2, laser; 3, incident beam; 4, beam reflected from the upper boundary; 5, beam reflected from the lower boundary; 6, photo detector; 7, lens; 8, etching solution.

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The dependence of thickness on etching time was calculated from interference curve and the dissolution rate υ (nm/s) as the slope of the curve was read.

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

Local optical-crystallization of $Sb_{20}Se_{80}$ thin films was carried out using He-Ne laser, λ = 633 nm and output energy 16mW for 30 min. The as-prepared samples were annealed at 85°C and 115°C up to 30 min in a normal atmosphere to produce the heat induced crystallization. Organic based solution e.g. amines was used for selective etching of optically crystallized/amorphous and thermally crystallized/amorphous thin films. To study the light induced interdiffusion, we irradiated the sample at room temperature by He-Ne laser of wavelength 633 nm with an intensity 15 mW.

III. Results

The amorphous $Sb_{20}Se_{80}$ thin film was crystallized in the area irradiated by laser beam. Locally optically crystallized/amorphous and thermally crystallized/amorphous thin films were selectively etched. The amorphous part is completely dissolved in the range of etching time 130 s, whilst the photo-crystallized and thermally crystallized area could be considered as insoluble as it is schematically depicted on Fig. 2 for optically induced crystallization. The etching rate of amorphous phase is 200 nm/s.

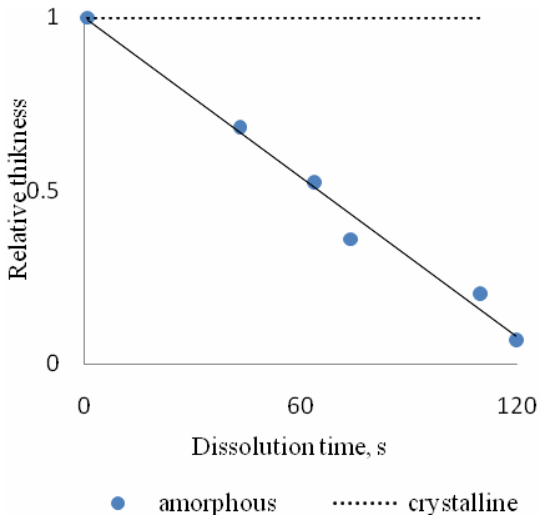


Fig. 2 Kinetics of dissolution of amorphous and crystalline phases of $Sb_{20}Se_{80}$ in organic etcher (room temperature)

It is well known that heating of SbxSe100-x films results in crystallization of the amorphous regions [13], [14]. Crystallization rate depends on the selected annealing temperature: the rate of crystallization is greater at a higher temperature. In order to characterize the etching process, the etch rate was obtained for as-deposited, crystallized and annealed $Sb_{20}Se_{80}$ thin films as a function of time (Fig.3). The change of the dissolution rate between amorphous and crystalline phase for $Sb_{20}Se_{80}$ thin films is connected with changes of the structure upon the illumination and/or annealing. Results show a pronounced decrease in the etch rate with an increase the degree of crystallinity right up to zero etch rate for crystalline phase.

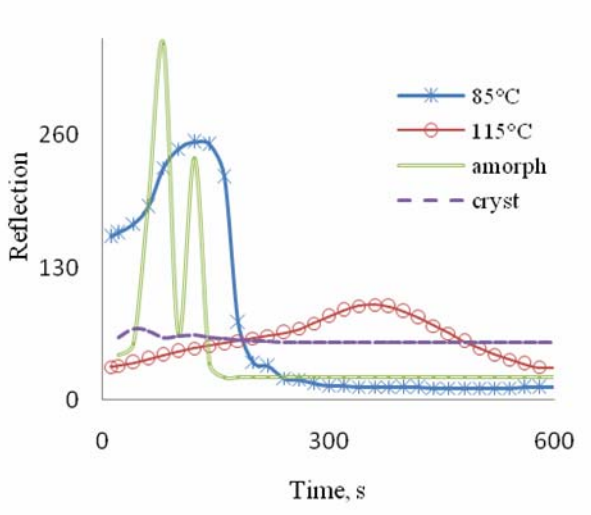


Fig. 3 Time dependent reflected signal during chemical etching of $Sb_{20}Se_{80}$ thin films (as-deposited/amorphous, crystalline, annealed at 85°C and 115°C)

Microanalysis shows significant change in composition between amorphous, crystallized not etched and crystallized selectively etched sample. Quantitative results taken on this specimen are listed in Table I.

TABLE I
Quantitative microanalysis with an Oxford INCA

Spectrum	Sb, at.%	Se, at.%	Sample description
Spectrum 1	20	80	As-deposited, amorphous
Spectrum 2	30	70	Cristallizsed, 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 sublimes [15], [16]. The percentage of antimony increases during the etching process as well. 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, remain unruptured during the etching process [17].

The growth of new crystalline phase in $Sb_{20}Se_{80}$ thin films during crystallization is shown in Fig. 4: spherulites (up to 60

μm in diameter) grow radially from the nucleation site, branching intermittently to maintain a space filling character.

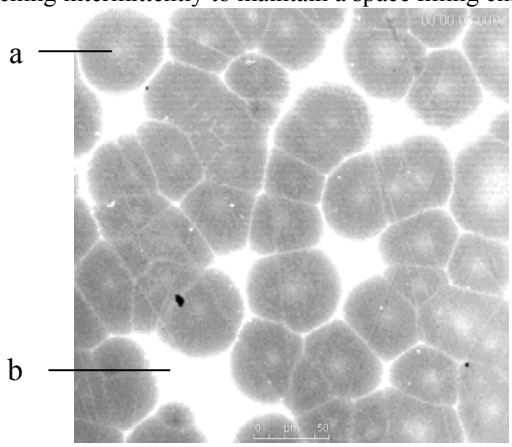


Fig. 4 The optical microscope image of new growing crystalline phase during the crystallization in $Sb_{20}Se_{80}$ thin films (a – spherulites, b – amorhous phase)

Thus, spherical crystallization patterns have arised at the beginning of the crystallization process. Further crystallization leads to the formation of the grains (Fig.5).

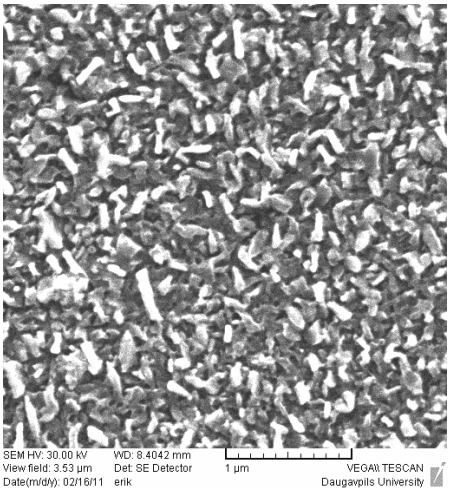


Fig. 5 SEM image of crystalline phase

IV. Discussion

In all the cases of selective etching of photo-crystallized and thermally crystallized $Sb_{20}Se_{80}$ thin films the amorphous phase was completely removed (dissolved) in etching solution contrary to crystalline one. The value of dissolution rate for studied amorphous thin films in organic etching solution is 200 nm/s. The dissolution rate of exposed thin films is decreasing with increasing the degree of crystallinity. The crystalline phase was proved to be insoluble within the dissolution time of amorphous phase (Fig. 2).

The time-resolved reflectivity change in the $Sb_{20}Se_{80}$ thin film may be observed from Fig. 3. The curve of amorphouse phase shows two peaks, that indicate the full completion of the etching process without any rest of thin film on the substrate.

The appearence only peak during the etching process in annealed samples shows that the crystallization process has not yet reached its saturation point: amorphous matrix was dissolved, but the crystalline area remained on the glass substrate.Crystallized area and crystalline rest after the etching were analyzed using EBSD to determine whether there are crystal grains. A close inspection of the EBSD image shows the presence of faint lines, several of which have been marked. As shown by J.A.Small lower quality EBSD images can usually be observed for particles less than about 1 μm in size. This is believed to be the result of a reduction in the intensity of diffracted electrons from the small particles due to the loss of electrons scattered out the particle sides and bottom [18]. Thus, we can assert, that polycrystalline material with the grains with size under 100 nm appears as the result of photo- and thermo crystallization. Spherulites are formed at the very initial stage of crystallization in $Sb_{20}Se_{80}$ thin films. In thin amorphous films spherulites are frequently observed during the first stage of crystallization [19], [20]. They occur as an intermediate and metastable, morphology which frequently may be recrystallized to form a fine-grained, randomly oriented, polycrystalline morphology (Fig. 4, 5). Using a number of methodologies (EBSD, microanalysis and XRD) the crystalline phase was determined as Sb, Se and stoichiometric $Sb_{40}Se_{60}$ composition. 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.

V. Conclusions

Selective etching of $Sb_{20}Se_{80}$ 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 $Sb_{20}Se_{80}$ 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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