Journal of Optoelectronics and Advanced Materials Vol. 3, No. 3, September 2001, p. 649 - 654

ELECTRON BEAM INDUCED PATTERNS IN Ag/GeS_4

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The results of a systematic study of the formation of patterns by an electron beam in GeS_4 are reported. A scanned electron beam has been shown to induce the dissolution of silver into the chalcogenide matrix in the irradiated areas. The dissolution produces an expansion of the material in the irradiated region that is believed to be due to the fact that the density of the reaction product is less than the average density of the silver and chalcogenide layers [11]. Once the chemical reaction was completed, no further migration of silver towards the irradiated area was observed in the Ag/GeS_4 thin films.

(Received June 6, 2001; accepted September 3, 2001)

Keywords: Ag/GeS_4, Electron beam irradiation, Silver dissolution and diffusion

1. Introduction

Glassy Ge_xS_{1-x} exhibits interesting properties in the presence of metals upon electron beam irradiation [1-3]. The dissolution of silver into chalcogenides assisted by UV light has been extensively studied by a number of researchers [1-4]. The most widely accepted model suggests that the incorporation of silver occurs as a result of the presence of a negative charge in the undoped region. The negative charge arises as a consequence of the generation of electron-hole pairs by UV light absorption. The holes, which have a higher mobility in chalcogenide glasses, diffuse towards the non-irradiated area, while the electrons are trapped in localized states. This gives rise to an electric field in the film, which is then enables cationic migration to occur [5].

Although much attention has been devoted to the dissolution of the metal by UV light, to the best of our knowledge few studies have been performed on the dissolution of silver in Ge_xS_{1-x} by electron beams [6,7]. Yoshikawa et al. [6] and Oldale and Elliot [7] have reported lateral diffusion of silver, dendritic deposition, crystallization and structural changes but the dissolution of silver in the amorphous matrix induced by electrons is still not well understood. This effect has potential applications in the patterning of GeS_4 by electron beams, because the doped compound is resistant to acid and alkaline solutions [8] making it easy to fabricate lines of sub-micrometre dimensions. The use of this system as an electron resist for mask fabrication is also possible.

2. Experimental

The chalcogenide glass was obtained by synthesis from the elements Ge and S (purity 99.99%) heated at 1000 ^{0}C for 18 hours in an evacuated silica ampoule and cooled by rapid quenching in an ice-water mixture [9]. A JEOL T220 secondary electron microscope (SEM), in which the electron beam was controlled by a computer, was used for electron beam writing, while the chemical composition of the material was analysed by energy dispersive x-ray analysis (EDX) in a JEOL T300 SEM equipped with an ANS 400 x-ray microanalysis system Thin films of the chalcogenide were obtained by physical vapor deposition. These films were investigated using a JEOL 100C transmission electron microscope (TEM) and were found to be amorphous.

Thin films of GeS_4 were deposited on a variety of substrates: silicon wafers, silicon wafers coated with silver, silica and silica coated with silver. The silica substrates were obtained through the reaction of oxygen with a polished silicon wafer, which resulted in a silicon substrate with a 0.5 μm thick silica film on top. To study the effect of the electron gun setup on the formation of the patterns, thin films were evaporated onto the substrates at a pressure of about 10^{-5} torr. The film thicknesses were about 200 nm for the chalcogenide and 20 nm for the silver layer. To study the characteristics of the silver dissolution into the chalcogenide matrix, more complex samples were produced. GeS_4 films

of 100 nm thickness were deposited on top of a 15 nm thick silver film, whereby the silver film was only underlying half of the GeS_4 film. For the removal of the chalcogenide film and the silver coating, a 0.1 M NaOH bath and 40% HNO_3 was used respectively. UV light exposures were performed using a high-pressure 200 W mercury lamp with the principal emission lines of around 370 nm and 435 nm. All patterns were analysed using a Dimension 3000 atomic force microscope (AFM).

3. Results and discussion

3.1 Silver dissolution in Ge-S assisted by electron irradiation

Two experiments have been designed in order to determine the mechanism of pattern formation on chalcogenide thin films that have been deposited onto silicon or silica substrates.

In the first experiment 15 nm of silver and 80 nm of GeS_4 were deposited in this order onto a silica substrate. The chemical composition of the chalcogenide films was analysed by x-ray microanalysis and confirmed to be $Ge_{20}S_{80}$. Patterns were written for different exposure times and with different electron gun set-ups. The chemical composition in the irradiated area was monitored during the electron beam irradiation and in all cases no change was observed in the silver concentration during the exposure. After the irradiation a set of line patterns could be observed on the surface.

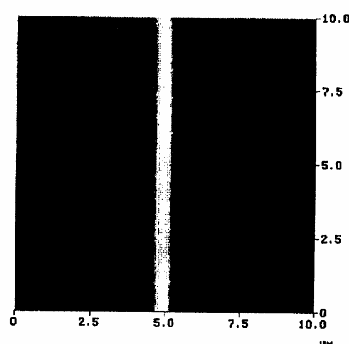

Fig. 1. AFM top view of a pattern written on a silica substrate after etching (Width = 0.4 μm).

The samples were then immersed in a NaOH bath for a few seconds. The material in the non-irradiated area was dissolved in the solution leaving the patterns unaffected. To remove the remaining silver, the surface was treated with a HNO_3 solution, which did not affect the structures. The dimensions of the patterns were measured in the AFM. Fig. 1 presents a top view of such a pattern created within 30 seconds at 15 kV and 0.5 nA.

It is believed that the electron beam induces a chemical reaction between silver and the chalcogenide in the irradiated area. The reaction product was found to be resistant to NaOH and HNO_3 solutions. Oldale et al. [4] and Eneva et al. [11] performed similar experiments using UV light and found that the reaction product has a fixed stoichiometry. This explains why no further increase in silver concentration was detected after the chemical reaction was completed.

For the second experiment a sample with the structure presented in Fig. 2 (10 nm silver and 130 nm GeS_4) was prepared. The chemical composition of the chalcogenide was $Ge_{20}S_{80}$. The sample was illuminated for 2 hours by a mercury lamp. After that time the sample experienced a colour change in the area where the silver was deposited (photodissolution [2-4]). A careful x-ray microanalysis was undertaken at the interface between the silver/chalcogenide and the chalcogenide. Silver x-ray peaks appeared only in the area where silver had been deposited but not in the areas where no silver had been deposited. It can therefore be concluded that UV radiation cannot induce lateral migration of silver towards the undoped region.

Subsequently, a set of lines was written across the interface using an electron beam of 20 kV accelerating voltage and 0.8 nA beam current. Exposure times for the lines were varied between 5 and 30 minutes. The whole sample was then introduced into a NaOH bath. The lines were not removed by the NaOH but all of the surrounding material was removed. This leads to the conclusion that the

scanned electron beam has induced a lateral migration of the silver towards the undoped region. The silver then reacted with the chalcogenide directly beneath the irradiated area and formed a reaction product which is resistant to alkaline solutions.

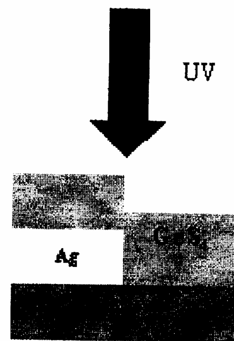

Fig. 2 Experimental setup to determine the lateral diffusion effect of silver.

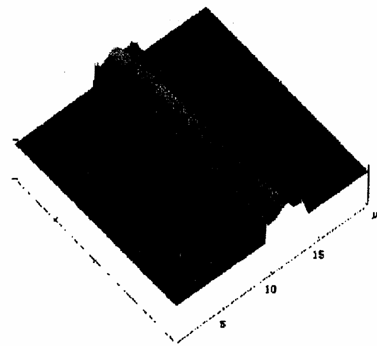

Fig. 3 AFM surface image of a pattern on a silica substrate after etching with NaOH. Width 4.3 μm, Height 154 nm.

Fig. 3 presents an AFM image of such a pattern written for 40 minutes after etching. Fig. 4 shows a section analysis from two patterns, the first one written for 5 minutes and the second one written for 30 minutes. All images were taken after the removal of the surrounding material. Fig. 3 and Fig. 4 show the effect of the electrons in the chalcogenide film. From these pictures it can be seen that there are two stages of the pattern formation. During the first stage silver is dissolved into the material without preserving the density. The second stage begins when the chemical reaction between the chalcogenide and the silver is completed. No more silver can be dissolved in the matrix and the deformation of the material occurs with the density being preserved. The first stage can be identified in the first picture of Fig. 4 and the second stage in the second picture of the same figure. The peripheral depression and the central expansion can be clearly distinguished in this picture.

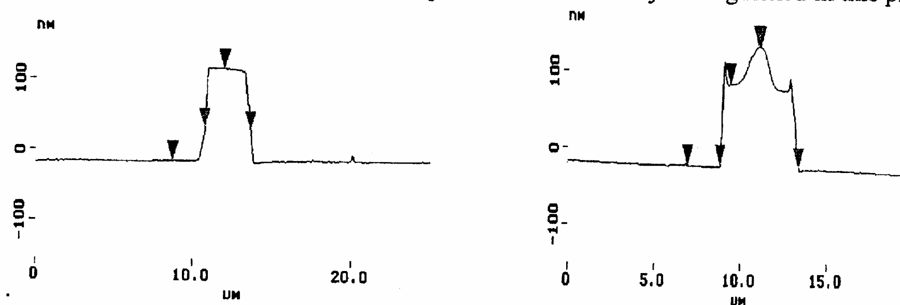

Fig. 4. AFM section analysis of line patterns drawn for 5 min and 30 min after etching in NaOH solution.

In order to clarify whether the continued irradiation with the electron beam could produce the precipitation of silver on the top of the features the sample was introduced into HNO_3, which can remove silver but not the doped material. The features were subsequently measured in the AFM but no changes in the dimensions of the lines were observed. This demonstrates that the electronic charge due to the electron beam can produce dissolution of silver but cannot attract silver ions to the surface of the pattern.

Fig. 5 shows the dependence of the thickness, the width and the volume of the patterns on the exposure time. In all the three cases it can be seen that the data can be fitted to a linear dependence. The slopes of the three graphs were calculated to be:

Width	2 nm/s
Thickness	0.02 nm/s
Volume	2.7 10^{-4} $\mu m^3/s$

This data shows that the increase in the volume of the patterns results principally from the increase in width. The observed results agree very well with the model proposed by Kokado et al. [5] for the dissolution of metals in amorphous chalcogenides assisted by UV light. In this model the metal-chalcogenide junction is considered to be a Schottky contact in which the silver cations are promoted into the chalcogenide when the junction is negatively biased by excited electrons that are trapped at dangling bonds. Similarly, the presence of electrons in the undoped chalcogenide film can bias the junction negatively, reinforcing the threshold field and attracting silver ions to the negative contact.

On the basis of this model and assuming that the interaction volume represents the negative contact, the increase in size of the patterns must be a consequence of the diffusion of electrons over time. From Fig. 5 it can be seen that the increase in width is the main cause of the increase of volume of the patterns. Since all lines, regardless of their exposure time, have the same length, which is very much larger than the width, the silver must migrate very quickly towards the irradiated area. Hence, the time constant for the recombination of silver ions with the electrons is much shorter than the exposure times used in the experiments. If it is assumed that once a steady state is established the incoming electrons produce a constant negative space charge in the film (interaction volume) and that the silver cations migrate towards this area in a very short time, then, the increase in the volume of the patterns must be a consequence of the spread of that space charge. From Fig. 5 it is clear that this space charge or interaction volume (mainly the width of this region) increases slowly with exposure time. This increase could be due to two mechanisms, the deflection of the main beam as a result of the surface being charged or the diffusion of the electrons towards the undoped region. The former mechanism has a low probability since the electrons have a high energy, the chalcogenide films are too thin and the silicon substrates have a relatively good conductivity. This makes the capacity for retaining charge limited. The latter effect is the more likely main mechanism for the increase in width of the features. It is believed that in the steady state the difference in electron density between the interaction volume and the surroundings will incur the diffusion of electrons into the surroundings, thereby increasing the size of the interaction volume and causing more silver to migrate into the newly created regions of electronic charge. This effect then leads to the broadening of the lines with exposure time.

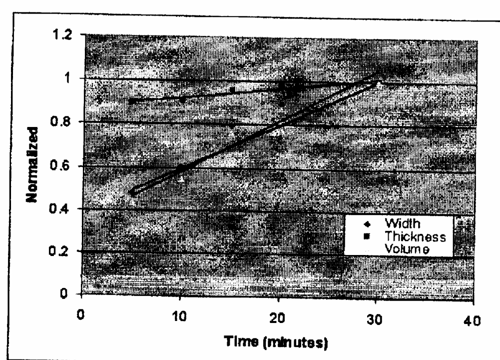

Fig. 5. Time dependence of the thickness, the width and the volume of the patterns.

3.2. Effect of accelerating voltage and beam current on the pattern formation

Thin films of 200 nm of GeS_4 and 20 nm of silver were deposited onto a silica substrate with the silver film underlying the GeS_4. A set of patterns was written on the surface using different electron gun set-ups. These patterns were subsequently measured in the AFM. All patterns were written for 5 minutes with an electron beam of 0.45 nA beam current. Fig. 6 shows the dependence of the thickness, the width and the volume of the patterns on the accelerating voltage. The y-axis is

normalized. The maximum values are 32 nm for the thickness and 820 nm for the width. The figure shows that the volume of the patterns decreases with increasing accelerating voltage. The specimen current was monitored during the exposure and is shown in Fig. 7. This figure shows that at 5 kV accelerating voltage the specimen current is only 30% of the beam current but this percentage increases at higher accelerating voltages. This indicates that at low accelerating voltages more electrons are retained in the sample increasing the density of electrons in the interaction volume, thus creating a stronger electrostatic field inside the film, which in turn increases the migration of silver ions towards the irradiated area. The minimum width obtained was around 0.5 μm.

Patterns were also written using different beam currents for the range of accelerating voltages used. Generally the volume of the lines has a maximum at a beam current of about 0.5 nA. This can be understood on the basis of the following model. Beam currents below about 0.5 nA cannot create a strong enough electric field to produce an effective dissolution of silver, whereas higher beam currents can overheat the sample and partially evaporate the material. The latter effect has been confirmed by irradiating samples with beam currents of high intensity. All features written with currents above 4 nA were valleys rather than hills for all accelerating voltages used.

Common characteristics of all patterns are that the thickness does not increase very much during long exposures and that the density does not remain constant as implied from the shapes of the electron beam generated patterns. These facts suggest that the formation of the patterns could be due to the expansion of the doped material. The incoming electrons induce the silver reaction with the chalcogenide. This chemical reaction is well-defined [4] and produces deformation of the surface because the density of the reaction product is lower than the average density of the initial silver and chalcogenide layers.

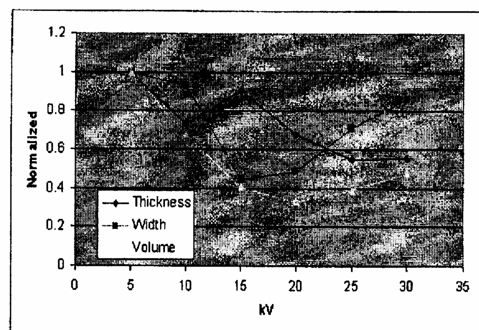

Fig. 6. Dependence of the thickness, the width and the volume on the accelerating voltage at a beam current of 0.4 nA and 5 minutes of irradiation.

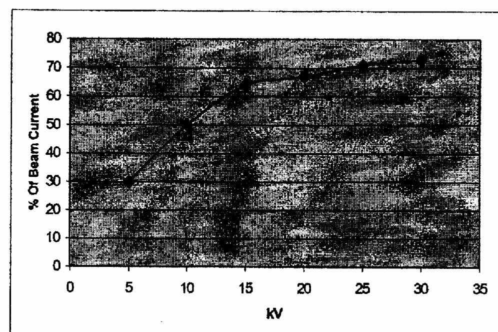

Fig. 7. Dependence of the specimen current on the accelerating voltage.

If this explanation is accepted then it appears logical that the use of a lower accelerating voltages produces the largest features. Lower accelerating voltages also give lower specimen currents [Fig. 7] and can therefore accumulate more charge for the same time of exposure and can hence produce the largest features.

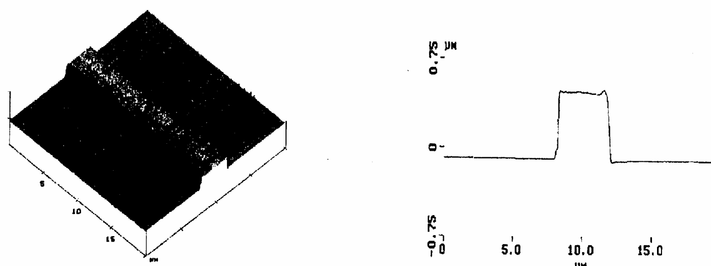

Fig. 8. Surface and profile of a pattern written on silicon with 5 minutes.at 15 kV of accelerating voltage and 0.5 nA of electron beam current. Width 4μm, Height 570 nm.

4. Conclusions

It has been shown that silver can be dissolved in GeS_4 by irradiation with UV light or by electron beam irradiation. Although the effects appear very similar, some important differences were observed. During UV light exposure, no lateral diffusion of silver was observed, while during electron beam exposure a lateral diffusion of silver took place.

It was demonstrated that fine line structures could be produced by scanning a focused electron beam across the surface of a Ag/GeS_4 sample. The formation of these patterns occurs in two stages. During the first stage the silver dissolves into the chalcogenide and forms a reaction product of fixed stoichoimetry, which is resistant to alkaline and acid solutions. The density of the reaction product in the irradiated area is less than the average density of the initial Ag/GeS_4 films and an expansion of the irradiated area occurs. Once the reaction between the chalcogenide and the silver is completed, the second stage commences. A further expansion of the irradiated area is observed, but now the density of the expanded area remains constant, and the expansion is now accompanied by a peripheral depression. During this stage no further migration of Ag was observed.

It was found that the highest features could be produced when using low accelerating voltages and an electron beam current of about 0.45 nA. The produced features were found to be resistant to alkaline and acid solutions. Therefore, these solutions can be used to remove the surrounding material, leaving the patterns unaffected and strongly attached to the substrate.

The effects described above demonstrate the potential application of the Ag/GeS_4 system in the fabrication of line structures.

Acknowledgements

The authors would like to thank EPSRC for the financial support of this project.

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