Structural study of Cu photodoped Ge-S glasses

M. BALAKRISHNAN[a], M. N. KOZICKI[a], C. POWELEIT[b], S. BHAGAT[c], T. L. ALFORD[c], M. MITKOVA[a,d*]

[a] *Center for Applied Nanoionics, Arizona State University, Tempe, AZ 85287-6206, USA*
[b] *Department of Physics, Arizona State University, Tempe, AZ 85287- 1504, USA*
[c] *School of Materials, Arizona State University, Tempe, AZ 85281- 8706, USA*
[c] *Department of Electrical & Computer Engineering, Boise State University, Boise, ID 83725-2075, USA*

The products formed by Cu photodiffusion in GeS_2 films are investigated. Rutherford backscattering spectrometry shows that for the experimental conditions used photodiffusion results in the introduction of 17.4 at. % Cu into the chalcogenide glass matrix. The diffusion product are analyzed by means of X-ray diffraction which reveals the formation of Cu_2GeS_3. Raman spectra show the considerable influence of Cu on the structure of the hosting glass which we relate to the incorporation of fourfold coordinated Cu into the glass matrix. Annealing of the films at 300^0C and 430^0C was also studied to determine the thermal stability of the ternary.

1. Introduction

The progress of microelectronics is paved by constant scaling and increasing of memory density. This is achieved partly by the application of new materials and device structures as well as advances in lithography. One of the most interesting contributions in the area of new memory devices is programmable metallization cell (PMC) memory technoogy which promises to meet all the requirements of the next generation of non-volatile memory [1]. It represents a radical departure from all other memory technologies in that it utilizes solid state electrochemistry with nanostructured materials to store data in a stable form at extremely low voltage and energy in a simple, ultra-scalable, embeddable structure. The electrolyte is formed by dissolving a metal (with Ag being the most common in this technolohy) in a chalcogenide or transition metal oxide glass. A metal (Ag)-containing layer and an inert electrode formed in contact with the electrolyte film creates a device in which information is stored via large resistance changes caused by the oxidation of the metal (Ag) and reduction of the mobile metal ions in the electrolyte. Polarity-dependent switching between the resistance states can occur within a few tens of nanoseconds for voltages of a few hundred mV and currents in the μA range. PMC possesses the endurance, retention, and CMOS compatibility required of advanced memory devices and has excellent scaling prospects due to the low operational power and physical scalability to the nanoscale regime [2].

Developments in microelectronic fabrication have allowed copper metal to be introduced in back-end-of-line (BEOL) processes. This has opened up new opportunities for PMC devices as the electrochemically active electrode may be made from the same Cu which already is used in the interconnecting layer above the Si circuitry, thus making the addition of PMC elements very cost effective.

The application of a Cu electrode requires the use of a solid electrolyte in the chalcogenide glasses that is doped with Cu and therefore the study of Cu-containing chalcogenide systems has become a priority.

The dominant understanding of the conductivity of Cu-containing glasses is that they do not show an ionic component and the mobility of Cu ions is lower than that of Ag ions.One could therefore expect these aspects to influence the performance of Cu-based PMC devices. The main differences in both metals are related to their ionic radii and coordination; these are Cu^+ (2) – 0.046 nm, Cu^+ (4) – 0.060 nm and Ag^+ (4) – 0.10 nm [3], where the figures in parentheses are the coordination numbers of the particular ions. From the position of the two elements in the Periodic table, one can conclude that Cu will have a stronger affinity to the chalcogens and indeed the bond-strengths for diatomic molecules are respectively 276 kJ/mol for Cu-S bond and 217 kJ/mol for Ag-S bond [3].

The chalcogenide system of particular interest is Ge-S doped with Cu since this hosting system offers potentailly high temperature stability compared to other chalcogenide hosting systems. While the Cu doped Ge-Se system is well documented [4,5], data about the Ge-S system are very scarce. Kawaguchi et al. [6] have studied co-evaporated GeS_2 – Cu films and have established that this mode of formation of these ternary films results in amorphous structures up to introduction of 62 at. %Cu. No phase separation was noted by the authors up to this Cu concentration. X-ray diffraction (XRD) data reveal formation of crystalline Cu when 65 at. % Cu has been co-evaporated. Same authors conclude from the IR spectra that with increasing Cu concentration up to 62 at. %, the formation of Cu-S bonds occur whose presence they deduce due to formation and development of an IR peak in the region 200-300 cm^{-1}.

In this work we report on the structures occurring after Cu photodiffusion in thin films of GeS_2 glasses. We

address both the changes taking place in the hosting chalcogenide backbone and the clusters containing copper. Furthermore, we investigate the influence of thermal annealing on the structure of the host and the size of the crystals of the diffusion products since in many actual applications the Cu-diffused chalcogenide glasses will undergo thermal processing. This work is part of our general materials characterization related to PMC technologies [2] to fill complete the picture of chalcogenide glass-metal systems on which PMC technology relies.

2. Experimental

Thin films (60 nm) were deposited by thermal evaporation at a vacuum of 10^{-6} Torr from previously synthesized GeS_2 glass using high purity elements. Although the starting source material is stoichiometric, dissociation occurs during the evaporation and the two elements evaporate with different rates due to their different partial vapor pressure. To preserve the composition of the film close to the source composition, a special evaporator was designed. This, in essence, is a semi-Knudsen cell with openings that are larger than the orifice of the Knudsen cell but small enough to ensure a reasonable evaporation rate, which was kept close to 1Å/sec. The source was mounted on the substrate normal axis and the angular separation of the source was reduced to assure symmetric and uniform flux distribution. To obtain more uniform composition profiles, the source to substrate distance was greater than 15 cm. Rotation was employed during deposition to even out the axial flux distributions.

A 30 nm thick copper film, which is transparent for the UV light used, was evaporated on top of the chalcogenide film. The given thickness combination of chalcogenide glass/copper was chosen to ensure saturation of the glass with Cu following photodiffusion, based on the results with Ge-Se glass [4]. The sandwich structure was evaporated onto Si wafers covered with SiO_2 to avoid Si – Ge inter- diffusion, which can take place during the processing used in this work [7]. This substrate was also preferred since it produces a low number of well defined signals in the characterization methods used that can be easily distinguished from the signals of the studied films. The formation of the solid electrolyte films was achieved by the same conditions as applied for the Ag-containing system in our previous efforts [8], illuminating the samples using a 405-436 nm wavelength of a mercury lamp. The power density was 5-5.3 mW/cm^2 and the illumination time applied was 20 minutes. The residual copper film was later etched in 1M solution of $Fe(NO_3)_3$ to reveal the surface of the doped ternary films for analysis. Some of these samples were thermally annealed in an inert gas ambient at 300^{0}C and 430^{0}C for 15 minutes. The anneal temperatures were chosen to represent "real world" back-end of line processing. The anneal temperature of 430^0 C is particularly important since this is the highest temperature used in most BEOL processes.

The composition of the films was studied using Rutherford Backscattering Spectrometry (RBS) carried out at the following conditions: He$^+$ ion beam with energy of 2MeV and diameter of 1mm and beam current at the target 18 to 20 nA. The sample was mounted with multiple axis goniometer control in a chamber evacuated to $7x10^{-7}$ Torr and surface barrier detection of backscattered ions was made at normal (180º) incidence and a backscattering angle 65º optimizing mass and depth resolution respectively. As the samples were quite beam sensitive, a reduced charge of approximately 0.25 mC/cm^2 was applied. Experimental RBS data were fitted with those obtained by numerical simulation using RUMP software [9].

The low temperature introduction of Cu into GeS_2 by means of photodiffusion differs from doping in the melt and co-evaporation, where the structure of the ternary compound depends on the chemical equilibrium of the glass component. In the case of photodiffusion, the thermodynamics of the reaction is such that the diffusion reaction products are nanocrystalline and they were therefore characterized using X-Ray Diffraction (XRD). The particular conditions in our study were as follows: the XRD was carried out under 1º glancing angle with CuK$_\alpha$ emission λ=0.15418 nm and a 2θ range from 10º to 60º with 0.002 degree step width and 1 sec/degree time per step. Total scanning time was 7 hrs. Identification of the crystalline phases of the diffusion products in the films was performed from the XRD analysis and the cluster sizes were calculated applying the commonly accepted formula for particle size using the Scherrer equation (1):

$$t = 0.9\lambda/B\cos\theta_B \qquad (1)$$

where t is the size (or particle size) of the crystal (in angstroms), λ the X-ray wavelength and θ$_B$ the Bragg angle. The line broadening, B, is measured from the peak width at half the peak height in radians. The particle size was obtained by averaging the data over each peak of particular composition.

To get a general idea about the changes occurring in the hosting films before and after the treatments, Raman scattering of the glass samples was obtained using the 514 nm line of an Ar$^+$ laser as the excitation source. Excitation was performed in the quasi-backscattering configuration with 15 mW average power and 100 micron spot size. The scattered light was collected and polarization selected through a half wave plate and Glan-Thompson polarizer. Edge filters were used to reject the Rayleigh scattered light from the input of the Acton SpectraPro275 monochromator which energy dispersed the collected signal onto a Princeton Instruments liquid nitrogen cooled CCD camera. The post acquisition analysis was performed with MicroCal Origin software and fitting routines.

3. Results

The RBS results revealed the composition of the Ge-S film to be $Ge_{34.37}S_{65.62}$ giving a Ge/S ratio of 1.91, i.e., the films were slightly enriched with Ge due to re-evaporation of S from the substrate during film deposition. The constituents forming the photodiffused films show their presence in three channels: 265-290 corresponds to copper, 275-295 to germanium, 205-220 to sulfur. The counts below 200 correspond to the substrate and they appear as a noise. The final composition of the films following copper diffusion in them was $Ge_{25.5}S_{57.1}Cu_{17.4}$. The amount of Cu introduced in the chalcogenide film is much lower than the amount of Ag that can be introduced using the same conditions – 17.4 at. % vs. 31 at.% [8]. One example of the RBS data for a copper-diffused Ge-S film annealed at 300^0 C is shown on Fig. 1. Although the peaks of Cu and Ge overlap they could be fitted well since they are sharp and well defined. There is an obvious appearance of a small peak at channel 225 which we assume corresponds to the occurrence of some chemical interaction between the elements in the system.
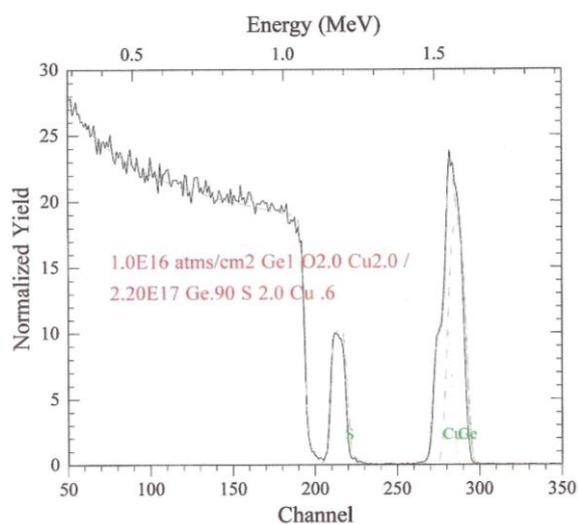

Fig. 1. RBS spectrum of a GeS2 film photodiffused with Cu and annealed at 300^0C.

The results from the XRD studies are shown on Fig. 2 a-c. They show that after diffusion, the material remains amorphous in the resolution limits of the instrument. While the Ge-S matrix remains amorphous after the thermal treatment at 300 ºC and 430 ºC, crystal formations related to Cu introduction in the Ge-S film were identified as being Cu_2GeS_3 using JCPDS card 89-2876. The crystal growth with the annealing is negligible – the average size of the crystals changes from 5.8 nm to 6.3 nm. Since the crystals were quite small and their signals were difficult to distinguish well, we performed a Lorentzian fit.
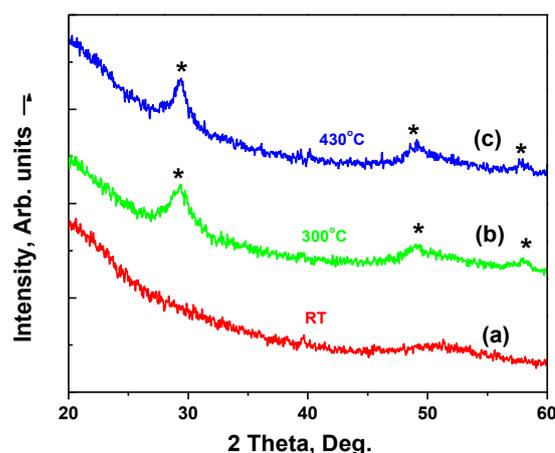

*Fig. 2. XRD data for films: (a) photodiffused with Cu GeS2 ; (b) photodiffused with Cu GeS2 annealed at 300^0C; (c) photodiffused with Cu GeS2 annealed at 430^0C; *denotes appearance of nano crystals from Cu2GeS3.*
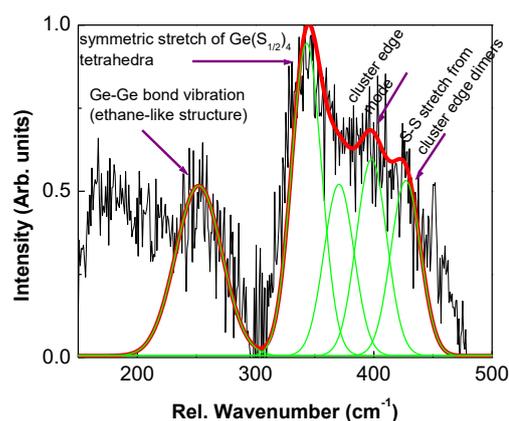

Fig. 3. Raman spectrum of a pure GeS2 film before Cu diffusion.

The Raman results for pure Ge-S films, Fig. 4a, show the appearance of a relatively high intensity mode at 343 cm^{-1} which was first identified by Lucovsky [10] and is generally accepted to represent the A_1 symmetric stretch of $Ge(S_{1/2})_4$ combined with scattering from the $Ge_2(S_{1/2})_6$ [11]. The two modes at 370 cm^{-1} and 427 cm^{-1} arise from the edge sharing structures [12]. There is a well resolved peak at 252 cm^{-1} corresponding to the vibrations coming from the ethane like structures available in glasses containing more than 33at.% Ge [11]. The deconvolution of the Raman modes between 340 and 440 cm^{-1} manifests the formation of a peak at 427cm^{-1}. This vibration mode is the subject of much discussion since many authors [11,13] relate it to the vibrations coming from S chains for which they have confirmation by other experimental techniques. However, computation based on density-functional theory [12] reports that it is due to the highest mode in the edge sharing cluster. We rather believe that this signal comes

from the vibrations of the S chains available due to the formation of wrong bonds in these glasses which are compensated by the appearance of Ge-Ge bonds.
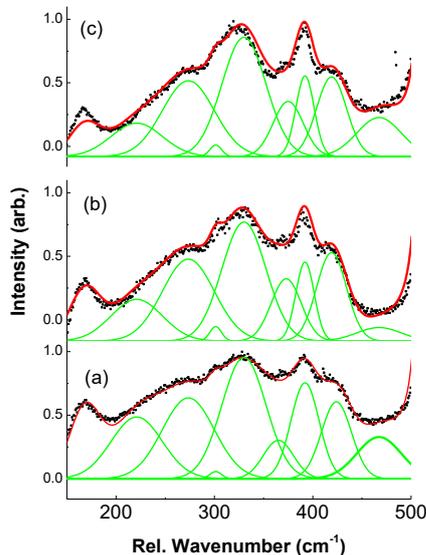

Fig. 4. Raman spectra for films: (a) photodiffused with Cu GeS₂ film; (b) photodiffused with Cu GeS₂ annealed at 300⁰C; (c) photodiffused with Cu GeS₂ annealed at 430⁰C;

Introduction of Cu drastically changes the structural organization of the material. The mode at 250 cm^{-1} appears to be dissipated in favor of modes at 223 and 275 cm^{-1}. Meanwhile, the cluster's edge mode at 294 cm-1 grows dramatically and its intensity complements the stretch mode of the Ge(S$_{1/2}$)$_4$ tetrahedra. Additionally, an supplemental mode at 470 cm^{-1} appears. The new-formed low energy 220-280 cm^{-1} modes correlate with CuS stretching modes and the 470 cm^{-1} peak also indicates the S-S stretching in a CuS structure. The mode that appears to manifest itself at 170 cm^{-1} is a lineshape due to the distortion from the Raman edge filter. It is considered to be part of the low energy boson peak [14] or other lower energy acoustic modes. Annealing temperature does not affect the shape and the presence of the particular structural units. We would like only to point out the decreasing intensity ratio $I(395 cm^{-1})/I(340 cm^{-1})$. For all these experiments we are able to track the mode at 300 cm^{-1} and 520 cm^{-1} coming from the Si substrate. Since these modes have almost the same intensity for all the spectra, we conclude the absorption is consistent in all samples.

4. Discussion

The structure of the hosting GeS₂ glass is well described (see for example 11) and, as we can conclude from the Raman spectrum of the GeS₂ film, it is characterized by the occurrence of some wrong bonds and the formation of ethane-like structures and sulfur chains.

Once this film is irradiated with band gap light, electron-hole pairs occur that produce metastable defects leading eventually to switching of covalent bonds as carriers recombine [15]. The switched covalent bond configuration leads to conditions which give rise of a photodiffusion as discussed by Fritzsche [16]. Since it has been established that at an illumination time longer than 15 minutes saturation of the effect occurs, [2,17] the process in our case was stopped after 20 minutes. Once Cu penetrates into GeS₂, it can react with S and there is a good variety of bonding and coordination that could occur. According to the lowest energy-bonding configuration arguments of Kastner [18], Cu is expected to form one normal covalent bond with a chalcogen atom. However, offering three empty s-p orbitals and being surrounded by lone-pair electrons of other chalcogen neighbors, the latter will move toward the Cu atom to form up to three coordinate bonds. The overall concentration ratio between the two types of bonding is determined by the law of mass action and entropy factor [18]. Because of the elecronegativity difference between Cu and the chalcogen elements, Cu is expected to become positively charged with the negative charge located on neighboring chalcogens, making the bonding complex overall neutral. 4-fold coordination is impossible or very rare for Ag due to sterric factors but Cu can be accommodated in the structure of the chalcogenide glass, becoming fourfold coordinated due to its smaller atomic radius. This advantage is especially important in the case of diffusion in Ge-S glass since its structure, compared to that of Ge-Se glass, offers narrower channels and accommodation space for the diffused ions because of the closer packed structure of Ge-S glass caused by the smaller S atom, shorter interatomic distances, and the lower level of polymerization of the structure [11]. However the high coordination of Cu is an inhibiting factor for the diffusion since this robust structure is not very flexible. This is the reason for the occurrence of limited photoinduced diffusion of Cu as revealed by the RBS analysis. Meanwhile, for Ag, if only one of the two sets of lone-pair electrons of the chalcogen defect C$^{-}_1$ forms a coordinate bond to Ag^{+}, the Ag^{+} can move to a new position neighboring the C$^{-}_1$ without breaking this coordinate bond because the two sets of lone pair-pair electrons can rotate in the plane normal to the covalent bond. The high coordination of Cu is also the reason for the apparent lack of ionic conductivity in ternary films, based on its inclusion in the chalcogenide glass, although the relatively low bonding energy of the Cu-S coordinative bond means that the formation of Cu^{+} is possible. In the case of photodoping, the matrix of the chalcogenide glass has been formed and fixed before the introduction of Cu. Therefore the possibility of creation of chemical bonds by metal atoms is determined beforehand and depends on the structure of this matrix. Hence, the chemical bonds between metal impurities and chalcogenide matrix are formed preferentially as coordinative bonds.

The fact that Cu can form entities with high coordination is the reason for the occurrence of a huge number of binary or ternary compositions following the reaction of Cu with S and with the Ge-S glass. The ternary

Cu_2GeS_3, which we have identified with XRD, is expected to crystallize in a monoclinic lattice [19]. It is isotypic with Cu_2SnS_3, a recently reported structure which can be viewed as a sphalerite super-structure [20]. In this structure, the Cu and Ge atoms occupy tetrahedral sites separately, though the tetrahedral units GeS_4, and two kinds of CuS_4 having considerable distortion from the regular tetrahedral forms with the size of GeS_4 being a little bit larger than the two kinds of CuS_4. The overall organization of the structure containing Cu_2GeS_3 requires the occurence of an adequate number of edge sharing units to account for the structure close to this of the crystalline compound. In this manner, the introduction of Cu into the GeS_2 breaks the Ge-Ge bonds and connects with S and it is for this reason that we witness simultaneously vanishing Ge-Ge and S-S modes on the Raman spectra of the photodiffused material. A similar effect has been reported by Tecklenburg at al. [21] by the introduction of Cu into Ge-Se glass, which the authors speculate could be related to the formation of Cu_3Ge. This can not be supported by the requirement for overall electroneutrality of the system; moreover the XRD results (Fig. 2) do not support the formation of Cu_3Ge. We can assume that the mode at 243 cm^{-1} which the authors believe is related to the Se-Se vibrations, is rather related to new units, since the breathing mode of Se chains usually occurs at 250-260 cm^{-1} [22].

One can expect that the introduction of a doping element into the GeS_2 matrix will increase the internal pressure in the network, although the $GeS_{4/2}$ clusters are much less strained probably due to their low dimensionality, compared to the $GeSe_{4/2}$ units. The experiments with external pressure over S rich Ge-S glasses doped with Sn [23] show a blue shift due to compressing of the interatomic bonds, which eventually converts into a red shift. This effect is explained with the instability of the tetrahedral bonding of the Sn atoms. One very important result related to the influence of the pressure effect is that the threshold pressure at which the blue shift occurs vanishes in the intermediate phase [22] but becomes higher with increasing rigidity of the glasses. When comparing the vibration modes of pure GeS_2 with those of Cu doped glasses (Fig. 3 and Fig, 4a-c), one realizes that the mode related to the Ge-Ge vibrations undergoes a tremendous blue shift. The modes at higher frequencies are not affected as much since in this case the fractional response decreases due to the restoring forces associated with higher mode frequencies which are larger, being more covalent in nature [22]. We even find a red shift in both modes related to the Ge-S tetrahedra which, however, should not be regarded as a sign of stress relief but rather must be related to the origin of Cu incorporation in the overall structure with the appearance of coordinative bonding. The picture of glass structure evolving due to Cu incorporation suggests that it is governed by internal stress which also prevents the crystal growth at elevated temperatures as revealed by the XRD study. There is a subtle difference in the Raman scattering cross sections as shown on Fig. 4 a-c which can easily vary by an order of magnitude from mode to mode, so that the observed mode scattering strengths do not necessarily reflect the bond statistics of the network.

Annealing temperature only appears to affect the linewidth of the 395 cm^{-1} mode. Upon annealing, the linewidth drops from about 28 to less than 18 cm^{-1}. However, given the overlap of the structural peaks and the fact that the sensitivity of the fits to the individual parameters is very coarse, the Raman spectra is limited in its full quantitative interpretation. For instance, the first principles calculations of Jackson et al [12] correlate a 366 cm^{-1} mode as also being associated with the ethane-like structure. If the Cu is breaking the Ge-Ge bonds then the 250 cm^{-1} as well as a 366 cm^{-1} range mode would be diminished. Therefore, the linewidth of the 395 cm^{-1} mode could seem to be narrowing but is actually due to a peak at 366 range being diminished so that the fits are not sufficiently sensitive to distinguish between the two effectively. We suggest that the growth of the scattering strength of the mode at 395 cm^{-1} arising from the cluster edges relative to that of the mode at 330 cm^{-1} (Fig. 5 a-c) is a evidence for the fractioning of the structure of the glass with the introduction of Cu and further annealing.

5. Conclusions

In this work, GeS_2 films photodiffused with Cu are investigated. The photodiffusion process results in relatively low (17 at. %) Cu concentration in the doped film, as compared to Ag photodiffusion in the same host. The Cu diffusion product is nano crystalline in nature with crystals of Cu_2GeS_3 forming. Annealing does not contribute significantly to their growth. We suggest that the high coordination of Cu and the close packing of the hosting backbone are the reasons for limited Cu diffusion and restricted growth of the crystals forming after diffusion. The hosting Ge-S backbone, which shows the presence of wrong bonds before the diffusion process, forms a new structural organization with significant development of cluster edge units caused by the inclusion of Cu and the formation of Cu_2GeS_3 . The new structure of the host following Cu photodiffusion appears to be much more fractioned compared to the structure of pure GeS_2.

References

[1] M. N. Kozicki, M. Mitkova, M. Park, M. Balakrishnan, C. Gopalan, Superlatt. and Microstr. **34**, 459 (2004) .

[2] M. N. Kozicki, M. Mitkova - J. Non-Cryst. Sol.**352**, 567 (2006).

[3] CRC handbook of Chemistry and Physics, David R. Lide Editor-in-Chief 81st Edition 2000- 2001.

[4] A. I. Stetsun, I. Z. Indutnyi, V. G. Kravets, J. Non-Cryst. Sol. **202**, 113 (1996).

[5] J. S. Romero, A. G. Fitzgerald, J. Appl. Phys. **93**, 4517 (2003).

[6] T. Kawaguchi, S.Maruno, S.R. Elliott, J. Non-Cyst. Sol. **204**, 83 (1996).

[7] M. Mitkova, M. N. Kozicki, H. C. Kim, T. L. Alford, Thin Solid Films, **449**, 248 (2004).

[8] M. Balakrishnan, M. N. Kozicki, C. D. Poweleit, S. Bhagat, T. L. Alford, M. Mitkova, J. Non-Cryst. Sol. **353**, 1454 (2007).

[9] L. R. Doolittle, Nucl. Instr. Methods Phys. Res. B **15**, 227 (1986).

[10] G. Lucovsky, F. L. Galeener, R. C. Keezer, R. H. Geils, H. A. Six, Physical Review B, **10**, 5134 (1974).

[11] P. Boolchand, J. Grothaus, M. Tenhover, M. A. Hazle, R. K. Grasselli, Phys. Rev. B **33**, 5421 (1986).

[12] K. Jackson, A. Briley, S. Grossman, D. V. Poresag, M. R. Pederson, Phys. Rev. B **60**, R14 985 (1999).

[13] H. Tao, S. Mao, G. Dong, H. Xiao, X. Zhao, Sol. State Communs., **137**, 408 (2006).

[14] Y. C. Boulmetis, A. Perakis, C. Raptis, D. Arsova, E. Vateva, D. Nesheva, E. Skordeva, J. Non-Cryst. Sol. **347** ,187 (2004).

[15] K. Shimakawa, A. Kolobov, S. R. Elliott, Adv. in Phys. **44**, 475 (1995).

[16] H. Firtzshe in P. Boolchand editor "Insulating and Semiconducting Glasses" World Scientific 2000, Singapore, New Jersey, London, Hong Kong pp. 653-690.

[17] F. Wang, P. Boolchand in G. Lucovsky and M. Popescu editors "Non-Crystalline Materials for Optoelectronics", INOE 2004, Bucharest, Chapter 2, pp 15-42. M. Kastner, Phil. Mag. B37, (1978) 127.

[18] L. M. de Chalbaud, G. D. de Delgado, J. M. Delgado, A. E. Mora, V. Sgaredo, Mat. Res. Bull, **23**, 1371 (1997).

[19] M. Onoda, X. Chen, A. Sato, H. Wada, Mat. Res. Bull, **35**, 1563 (2000).

[20] Mary M. J. Tecklenburg, Elizabeth Larsen, Bogdan Lita, Didarul Islam Qadir, J. Non-Cryst. Sol. **328**, 40 (2003).

[21] Fei Wang, S. Mamedov, P. Boolchand, B. Goodman, M. Chandrasekhar, Phys. Rev. B, **71**, 174201 (2005).

[22] K. Murase, T. Fukunaga, K. Yakushiji, T. Yoshimi, I. Yunoki, J. Non-Cryst. Sol., **59&60**, 883 (1983).

_____

*Corresponding author: mariamitkova@boisestate.edu