

---

This paper was awarded in the V International Competition (1996/97) "First Step to Nobel Prize in Physics" and published in the competition proceedings (*Acta Phys. Pol. A* **93** Supplement, S-29 (1998)). The paper is reproduced here due to kind agreement of the Editorial Board of "Acta Physica Polonica A".

---

# INFLUENCE OF LIGHT ON DISSOLUTION PROCESSES IN CHALCOGENIDE GLASSY SEMICONDUCTORS

D. BOYARSKIY

Mivza Ovda 110/28, Beer Sheva, Israel

## Abstract

In this work characteristics of dissolution processes in chalcogenide glassy semiconductors (illuminated and non-illuminated) were studied. The main purpose of this work was studying different compounds of the chalcogenide glassy semiconductors of the As–Se and As–S systems and their reciprocation with some selective solvents. The author of this document and his instructor consider as the most significant result of this work the discovery of an effective positive solvent ( $\gamma \approx 100$ ) in  $\text{As}_{45}\text{S}_{55}$  films.

PACS numbers: 71.55.Jv, 78.90.+t

## 1 Introduction

Chalcogenide glassy semiconductors, in brief ChGS, are a wide group of glassy alloys of chalcogenide (Te, S, Se) with other elements — foremost with Sb, Ge, As [1].

ChGS have several properties common to regular semiconductors. For example, a rise in temperature causes their resistance to decrease while a decline in temperature causes the resistance to increase [1]. They exhibit photoconductivity, i.e., their electrical resistance varies under the influence of light [1]. They exhibit other phenomena typical of semiconductors. By changing the composition of ChGS it is possible to change their electrical, optical and physicochemical properties within a wide range.

ChGS also have properties distinguishing them from other regular semiconductors. For example, their electrical properties are almost independent of doping materials. The electric charge carriers within ChGS are exclusively holes [1]. One of the most interesting and important effects which happen in ChGS is the change of certain physical and chemical characteristics under the influence of light. For example, the area of the membrane on a glass plate illuminated by light will dissolve in certain materials quicker than that part of the membrane not exposed to the light, while in other materials it dissolves slower. Likewise the exposed area becomes darker. These changes, induced by light, are reversible, i.e., it is possible to return the membrane to the same state in which it was before being exposed. This may be done by heating the exposed area to its melting point [1]. The changes in the properties described above are due to the change in membranes structure under the influence of light [1]. These structural changes are caused by the removal of electrons participating in interatomic bonds by quanta of light. The weakening of these bonds causes a distancing of atoms whose common bonding has weakened and this causes a change in the structure of the material. The distancing happens because of thermal vibrations of the atoms. Heating causes the original bonds to be restored and therefore restores the initial structure. The original properties are also restored.

Due to the above phenomena caused by light it is possible to use ChGS in various areas within industry, for example microelectronics, optoelectronics, non-silver photography and in particular in the writing and storage of optical data (high resolution up to  $10^4$  per mm) [1, 2].

From what has been described above it is clear that ChGS are inorganic photoresists (as opposed to the organic photoresists, polymers, which have a wide range of use in the microelectronics industry). Different solutions, which we use in experiments during the course of our work, destroy more effectively the bonds in the illuminated area. We refer to these as positive solutions. Others destroy more effectively the bonds in the non-illuminated area. We call these negative solutions.

The process of dissolution of the ChGS membranes can be characterized by a contrast  $\gamma$ , i.e. by the relation between the speed of dissolution of the illuminated area to that of the non-illuminated area or vice versa such that  $\gamma$  is never smaller than 1. The efficiency of the photolithographic process is improved the greater  $\gamma$  is.

As opposed to photoresists in use today, which do not require a long illumination time in order to change the structure of the exposed area (an exposure of several seconds is sufficient), ChGS photoresists require a strong and sustained illumination, which can be obtained from a quantum optical generator — a laser, a mercury lamp, or another strong light source. Aside from this, different compositions of ChGS are sensitive to different parts of the light spectrum. There are ChGS sensitive to wavelengths within the visible portion of the spectrum. Others are sensitive to wavelengths of IR or UV light.

As of now, when the study of the change of dissolution is far from complete, no selective effective solvents for the various ChGS have been found. In particular, none has been found for photoresists based on As–Se, As–S. If, for example, effective negative solvents are known today, the positive ones can produce only a very small contrast  $\gamma$  ( $\gamma \leq 2$ ).

As for ChGS photoresists As–S, today we know more or less about the  $As_2S_3$  [3] photoresists, while other compounds of the As–S system have not been researched. For the above-mentioned reasons, we see as the purpose of our work to study other compounds of ChGS of the As–S and As–Se and their reciprocation with other selective solvents.

## 2. Method of scientific research

All types of ChGS photoresists are actually membranes of thickness 0.2–1.0  $\mu\text{m}$  which are produced in our laboratory by the method of evaporating the appropriate ChGS material on clear glass plates or clear plates from polymer membranes in a vacuum.

The ChGS membrane under study is illuminated, for a certain duration, by laser light or by a mercury lamp (a particular area within the ChGS is illuminated).

In our experiments we used a laser manufactured by UNIFAX, which generated a narrow (0.36 mm radius) monochromatic beam whose wavelength was  $l = 633$  nm. The power output of the laser was  $w = 10$  mW. This light was absorbed very efficiently by As–Se type ChGS, and caused structural changes in the illuminated area (the illuminated area became darker). As–S type ChGS membranes tend to absorb very little light of wavelength  $l = 633$  nm and therefore we used a mercury lamp whose output is  $w = 250$  W or illuminated them with sunlight.

In order to research the dissolving process of ChGS we used two methods. The first, so-called abstract method, employs visual determination (by eyesight and with no instruments whatsoever) of the entire dissolution time duration of the illuminated area and the non-illuminated area of the ChGS membrane. It is not difficult to perform experiments and analysis under the first method because all of the researched membranes have a red or yellow hue. Therefore, it is easy to determine the entire dissolving time because as the membrane dissolves the clear plate remains and in that place no color is detected.

After we determined the entire dissolving time of the illuminated area ( $T_{\text{exp}}$ ) and of the non-illuminated area ( $T_{\text{unexp}}$ ) we can calculate the value of the contrast  $\gamma$  as the ratio of the dissolving time of the illuminated area to the non-illuminated area.

In the second method we must use an instrument described in [4]. A He–Ne laser generates, as described before, a light beam which is reduced by an attenuator and impinges upon the ChGS membrane in a solution in a beaker. Because of the phenomenon of interference, the light intensity is increased or decreased and is detected by a photodiode. This sensor generates a signal whose magnitude is directly proportional to the intensity of the detected light. This signal is recorded in a data recorder, and the data recorder “draws” the signal as a function of time  $I(t)$ .

In order to determine the rate of the dissolution of the ChGS membrane, we can use the interference equation which in our case relates: the wavelength  $\lambda$ , the index of refraction  $n$  and the thickness of the film  $D$ :

$$(2D)n = m(\lambda), \quad m = 1, 2, 3 \dots \quad (1)$$

For the first maximum we obtain:  $(2D_1)n = m(\lambda)$ . For the second maximum we obtain:  $(2D_2)n = (m + 1)(\lambda)$ . From those two equations we obtain:  $|D_2 - D_1| = \lambda/(2n)$ .

Now that we are aware of the equation  $|D_2 - D_1| = \lambda/(2n)$ , we may calculate the speed of dissolution, since in the time interval between two maxima or two minima an area of thickness  $|D_2 - D_1|$  dissolved and so the rate of dissolving is

$$V = |D_2 - D_1|/\Delta t$$

Now we can calculate  $\gamma$ . The rate of dissolving of the illuminated area is  $V_{\text{ill}} = |D_2 - D_1|/\Delta t_{\text{ill}}$ , while that of the non-illuminated area is:  $V_{\text{nonill}} = |D_2 - D_1|/\Delta t_{\text{nonill}}$  and so  $\gamma = V_{\text{ill}}/V_{\text{nonill}} = \Delta t_{\text{nonill}}/\Delta t_{\text{ill}}$ .

### 3. Experimental results

#### 3.1. Experiments done with abstract method

The first two experiments were performed in order to investigate the process of dissolution of As–Se ChGS membranes on polymer plates, in a KOH solvent. The membranes were illuminated with a He–Ne light source.

The first experiment was performed to investigate the dependence of  $\gamma$  on the concentration of the solvent. Table I which contains the results of this experiment includes the dissolution time of the illuminated ( $T_{\text{exp}}$ ) and non-illuminated ( $T_{\text{unexp}}$ ) areas, the average dissolution time of the illuminated areas ( $T_{\text{expavr}}$ ) and non-illuminated areas ( $T_{\text{unexpavr}}$ ) — in the event that two or more experiments were conducted, and the average values for  $\gamma$ .

**Table I.** Dissolution parameters for As–Se membrane in KOH solution with various solvent concentrations.

Concentrate of solvent in solution [%]	7.5	10	15
$T_{\text{exp}}$ [s]	80	22.5, 21	8, 9
$T_{\text{unexp}}$ [s]	636	200, 202	60, 80
$T_{\text{expavr}}$ [s]	80	22	8.5
$T_{\text{unexpavr}}$ [s]	636	201	70
$\gamma_{(\text{avr})}$	7.95	9.14	8.24

From the data in Table I it is evident that the concentration of the solvent in a solution does not have a strong effect on the contrast  $\gamma$  in the range of concentrations investigated. It is hard to produce the solvent concentration above 15% because the solute KOH does not mix with water. But we see from Table I that the dissolving time of the exposed and non-exposed area decreases with the increase in concentration.

The second experiment was conducted to establish a relation between the thickness of the membrane and the contrast  $\gamma$ . The solvent concentration was 10%. The membranes were illuminated by He–Ne laser light. Table II provides the results of the experiment.

**Table II.** Dissolution parameters for As–Se membrane in KOH solution as a function of membrane thickness.

	$d = 2.84 \mu\text{m}$			$d = 0.946 \mu\text{m}$	
$T_{\text{unexp}}$ [s]	105	115	110	80	85
$T_{\text{exp}}$ [s]	25	33	30	18	22
$\gamma$	4.2	3.5	3.7	4.4	3.86
$\gamma_{(\text{avr})}$	3.8			4.13	

**Table III.** Comparison of dissolution parameters for  $\text{As}_2\text{S}_3$  membrane in “A” and KOH solutions with the some solvent concentrations.

$T_{\text{unexp}}$ [s]	10	11	13	30	65	75
$T_{\text{exp}}$ [s]	135	137	135	45	35	45
$\gamma$	13.5	12.45	10.38	1.78	1.86	1.67
$\gamma_{(\text{avr})}$	12.11			1.77		
Solvent	Solvent “A” 0.5%			KOH 0.5%		

As we see from the results of the experiment, the thickness of the membrane  $d$  has a negligible effect on the value of  $\gamma$ . The question is, why the value of  $\gamma$  in experiment 1 is different than that obtained in experiment 2? Apparently, the difference is due to the fact that in the first experiment the membrane was created a short while before whereas in the second experiment the membrane used was five years old. In such a time period, physical and chemical properties of the material may have changed — influencing the value of  $\gamma$ .

Two other experiments were conducted with the  $\text{As}_2\text{S}_3$  ChGS membrane on polymer and glass plates. Table III was compiled according to the results of the third experiment which compared the value of  $\gamma$  of the  $\text{As}_2\text{S}_3$  membrane between a negative solution which we shall call solvent “A” (the compounds of this solution are secret and known only by Professor Victor Lyubin from the Department of Physics in Ben Gurion University in Israel) and a KOH solution which is positive. The membranes were illuminated with a mercury lamp.

As we see in Table III, the contrast  $\gamma$  obtained when solvent “A” is used is several times greater than that when KOH is used. Table IV presents the results of an experiment determining the difference between the effect of sunlight and a mercury lamp on the  $\text{As}_2\text{S}_3$  membrane in a negative solvent (solvent “A”).

**Table IV.** Comparison of dissolution parameters for  $\text{As}_2\text{S}_3$  membrane in solvent “A” for various sources of light.

$T_{\text{unexp}}$ [s]	30	25	30	18	20	6	4	3
$T_{\text{exp}}$ [s]	140	110	115	100	100	30	33	45
$\gamma$	4.7	4.4	3.83	5.56	5	5	8.25	10
$\gamma_{(\text{avr})}$	4.7					7.75		
Light source	sun					mercury lamp		

As is apparent from the results of the experiment, the values of  $\gamma$  in  $\text{As}_2\text{S}_3$  membranes that were illuminated by sunlight were smaller than those illuminated by the mercury lamp. In addition, there are differences in dissolution times, particularly in those areas which were not illuminated. We think that these are due to the dissolution of the membrane during the exposure to the sunlight, which caused a change in the structure of the membrane. We also tested the effect of propylamine on the  $\text{As}_2\text{S}_3$  membrane. The concentration of the solvent was

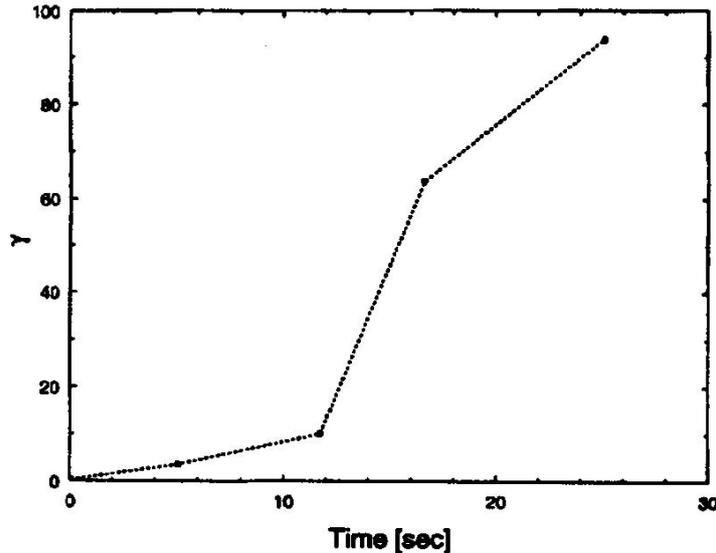


Fig. 1. Graph showing the contrast  $\gamma$  as a function of illumination time of  $\text{As}_{45}\text{S}_{55}$  membranes dissolving in solvent “A” 0.25%.

25%, the dissolution time of the membrane in the solvent was about two minutes with  $\gamma \approx 1$ . After obtaining those results we stopped using propylamine. We tried as well using  $\text{Na}_2\text{HPO}_4$  as a solvent but it had no effect on the  $\text{As}_2\text{S}_3$  membrane and so we stopped using it, too.

Along with the  $\text{AsSe}$  and  $\text{As}_2\text{S}_3$  membranes, which were investigated in the past, we investigated  $\text{As}_{45}\text{S}_{55}$  membranes, which were never previously researched. We were aware of the fact that a slight change in the composition of the membrane ( $\text{As}_{40}\text{S}_{60}$  ( $\text{As}_2\text{S}_3$ ) and  $\text{As}_{45}\text{S}_{55}$ ) could bring about a significant change in the physical and chemical properties of the membrane [5]. We tried dissolving the  $\text{As}_{45}\text{S}_{55}$  membrane in the negative solvent “A”. In the first experiment the membrane was illuminated by sunlight for one hour. The concentrations of the solvent were 0.25% and 8%. The results are presented in Table V.

**Table V.** Dissolution parameters for  $\text{As}_{45}\text{S}_{55}$  membrane in solvent “A” for two different solvent concentrations.

$T_{\text{unexp}}$ [s]	110	110	115	1834	1626
$T_{\text{exp}}$ [s]	1.6	1.6	1.8	18.7	16
$\gamma$	68.75	68.75	63.89	98	101.63
$\gamma_{(\text{avr})}$	67.13			99.82	
Concentration of solvent [%]	8			0.25	

In this experiment two interesting things were discovered:

1. A solvent which was negative (for  $\text{As}_{40}\text{S}_{60}$  and  $\text{AsSe}$  membranes) became positive for  $\text{As}_{45}\text{S}_{55}$ .
2. Solvent “A” provides a very high  $\gamma$  for  $\text{As}_{45}\text{S}_{55}$  membranes.

As a result of the first experiment we decided to conduct two more experiments to determine the relation between illumination time and  $\gamma$ . The second experiment (with  $\text{As}_{45}\text{S}_{55}$  membranes) was performed with solvent “A” — 0.25% and the membranes were illuminated with a mercury lamp. The results are recorded in Table VI and described by the graph in Fig. 1.

The second experiment was performed with the same membranes and solvents but this time the membranes were illuminated by sunlight.

The results of the first and of the second experiment show an increase in the value of  $\gamma$  as illumination time increases.

**Table VI.** Dissolution parameters for  $\text{As}_{45}\text{S}_{55}$  membrane in solvent “A” illuminated with mercury lamp as a function of illumination time.

Illumination time [s]	0	300	700	1000	1500
$T_{\text{unexp}}$ [s]	1275	1275	1275	1275	1275
$T_{\text{exp}}$ [s]	1275	365	127	20	13.5
$\gamma$	1	3.49	10	63.75	94.44

**Table VII.** Dissolution parameters for  $\text{As}_{45}\text{S}_{55}$  membrane in solvent “A” illuminated by sunlight as a function of illumination time.

Illumination time [s]	0	120	300	420	600	3600
$T_{\text{unexp}}$ [s]	1380	1380	1380	1380	1380	1380
$T_{\text{exp}}$ [s]	1380	385	280	150	90	17.35
$\gamma$	1	3.58	4.93	9.2	15.33	79.54

### 3.2. Investigating of the dissolving process of $\text{As}_2\text{S}_3$ membranes by means of a device

Figure 2 shows a curve, obtained through the recorder, that describes the dissolving process of the non-illuminated  $\text{As}_2\text{S}_3$  membrane of thickness  $D = 0.65 \mu\text{m}$ , in solvent “A” 0.5%. It is evident that the rate of dissolution is constant in time and that the final dissolution time is  $T_{\text{unexp}} \approx 10$  s. Figure 3 shows a (computer processed) graph that describes the dissolution process of an illuminated  $\text{As}_2\text{S}_3$  membrane. The illumination time was thirty minutes and the illumination was made by a mercury lamp. By our convention, the maximum intensity impinging upon the photodiode was assigned 1 and the minimum intensity was assigned 0.

From Eq. (1) which we obtained in the previous section describing the methods of research, we know that the thickness of the membrane dissolving between two extrema of interference equals  $D = m\lambda/(4n)$ , where  $m = 1, 2, 3 \dots$  (integer),  $n$  (index of refraction of  $\text{As}_2\text{S}_3$  membrane) = 2.3,  $\lambda$  (wavelength of laser light) =  $0.6328 \mu\text{m}$ .

By substituting the values into the equation we obtain  $D = 0.0688 \mu\text{m}$ . We count extrema from the moment the thickness equals zero, see Fig. 2. From this equation and from the graphs in Figs. 2 and 3 we obtain the following table (for non-illuminated  $\text{As}_2\text{S}_3$  membranes):

**Table VIII.** Dissolution parameters for  $\text{As}_2\text{S}_3$  membrane in 0.5% solvent “A” (details in text).

$M$	$D$ [ $\mu\text{m}$ ]	$T_{\text{exp}}$ [s]	$T_{\text{unexp}}$ [s]
9	0.619	31	0.625
8	0.550	52	1.625
7	0.481	70	2.125
6	0.412	82	3.250
5	0.344	92	4.000
4	0.275	101	5.125
3	0.206	108	6.250
2	0.138	115	7.875
1	0.069	125	9.625

Using the data in Table VIII, we can compile a graph depicting membrane thickness (illuminated and non-illuminated areas) as a function of time. This graph is shown in Fig. 4. We see there that the rate of dissolution of the illuminated area increases with time. This is due to the nonuniform illumination of the membrane. The upper layers of the membrane are more heavily illuminated than the lower layers and so therefore the rate of dissolution of the lower layers is greater than that of the upper ones. From that graph we also see that the values of  $\gamma$  in the initial areas equal 30 to 50, while the value in the final areas of dissolution equals approximately 12.

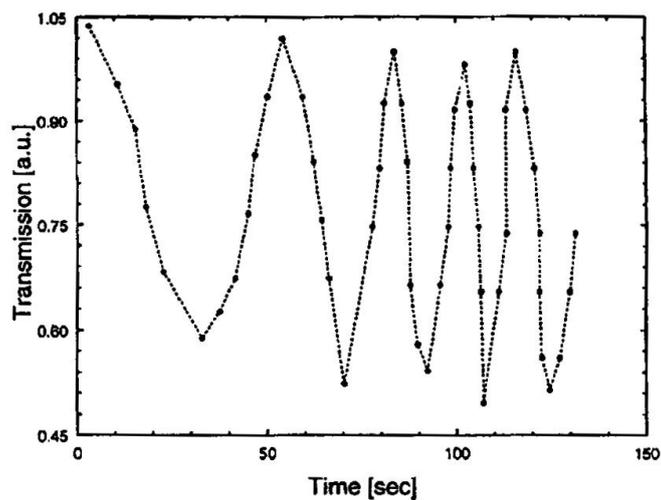


Fig. 2. Graph showing the light intensity traversing the non-illuminated  $\text{As}_2\text{S}_3$  membrane impinging upon the photodiode, as a function of time (negative solvent "A"). The time interval between two adjacent lines equals 5 s.

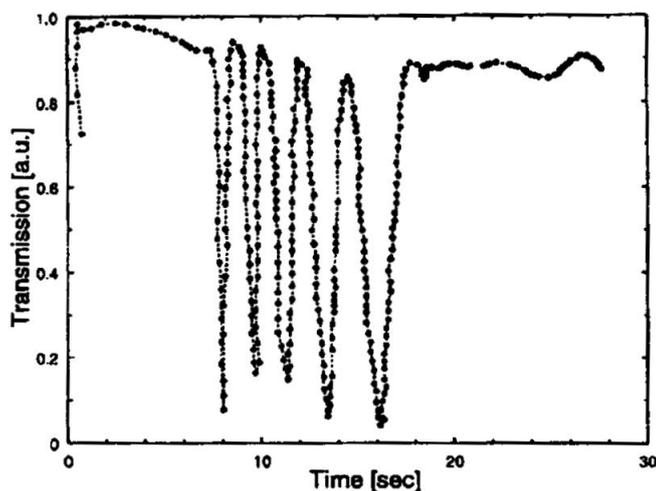


Fig. 3. The graph shows the change in light intensity traversing the illuminated  $\text{As}_2\text{S}_3$  membrane dissolving in solvent "A" 0.5% as a function of time.

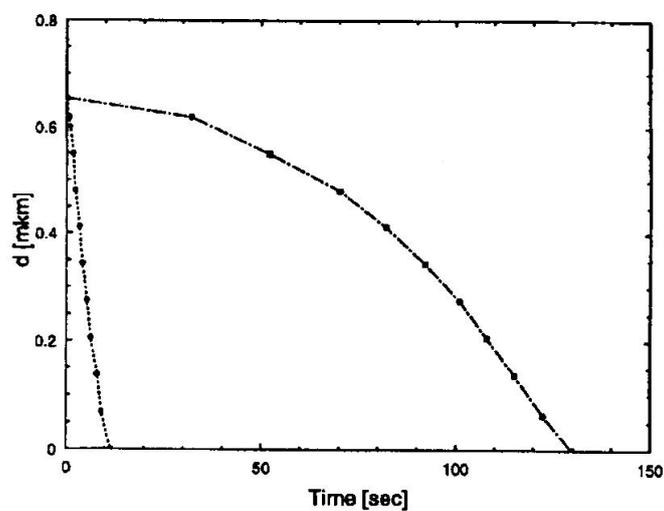


Fig. 4. Kinetics of the dissolution of non-illuminated  $\text{As}_2\text{S}_3$  membranes (1) and ones illuminated by a mercury arc lamp for 25 minutes (2) as a function of time in a negative solvent.

### 3.3. As<sub>45</sub>S<sub>55</sub> membranes

We illuminated the As<sub>45</sub>S<sub>55</sub> membrane with a mercury lamp for a half an hour. The results of the experiment, in which we dissolved the membrane with the “A” solvent, are shown in Fig. 5.

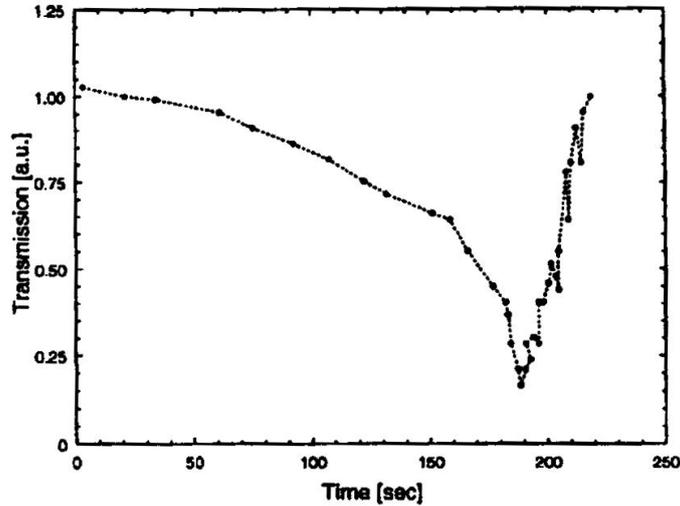


Fig. 5. The graph shows the change in light intensity traversing the illuminated As<sub>45</sub>S<sub>55</sub> membrane dissolving in solvent “A”, as a function of dissolution time.

By our convention, the maximum intensity impinging upon the photodiode was assigned 1 and the minimum intensity was assigned 0. We could not see the interference pattern because of scattering effects of the membrane on the laser light. We could visually detect the scattering. Apparently, this phenomenon is due to nonuniform dissolution of the membrane. This is probably due to an accumulation of excess arsenic (As). Because of the nonuniform dissolution, the upper layer of the membrane becomes porous and scatters the light. We attempted to stir the solution during the dissolution period, but this did not sufficiently reduce the scattering.

Due to the scattering of light in As<sub>45</sub>S<sub>55</sub> membranes, we can rely only, to our consternation, on the results obtained using the abstract method.

## 4. Summary of the results

1. The contrast  $\gamma$  is practically independent of the concentration of the solvent within the investigated range of AsSe membranes. The dissolution times of the illuminated and non-illuminated membranes decrease as the concentration of solvent increases.
2. A change in membrane thickness has virtually no impact on  $\gamma$  within the investigated range.
3. The values of  $\gamma$  for As<sub>2</sub>S<sub>3</sub> membranes in a negative solution “A” are far greater than those for the same membranes in a KOH solvent. These results comply to the results in the literature.
4. Illuminating As<sub>2</sub>S<sub>3</sub> and As<sub>45</sub>S<sub>55</sub> membranes with a mercury lamp yields values of  $\gamma$  greater than those obtained when illuminating with sunlight.
5. We showed that the solvent “A”, while negative for As<sub>2</sub>S<sub>3</sub> membranes, became positive and gave a value of  $\gamma$  close to 100 in As<sub>45</sub>S<sub>55</sub> membranes.
6. The dependence of  $\gamma$  on illuminating times of As<sub>45</sub>S<sub>55</sub> membranes in a negative solution was studied.
7. In the second method we verified results obtained by the first abstract method for As<sub>2</sub>S<sub>3</sub> membranes and we also observed the entire dissolution process of the membrane. These experiments also showed that the illuminated membranes dissolve at a non-constant rate because of the inconsistent absorption of the mercury lamp light within the entire membrane.

8. During the dissolution process of  $\text{As}_{45}\text{S}_{55}$  membranes (in the second method) a scattering phenomenon was discovered which is due to, apparently, the unhomogeneous distribution of excess arsenic in the membrane.

In our opinion the most significant result of this work is the discovery of an effective positive solvent ( $\gamma \approx 100$ ) in  $\text{As}_{45}\text{S}_{55}$  membranes.

## Acknowledgments

I would like to give special thanks to my instructor, Professor Victor Lyubin from the Department of Physics in Ben Gurion University in Israel, from whom I received a great help in everything and who suffered me for a long time, to Dr. Matvey Klebanov who helped me to deal with an equipment, to Dr. Witold Daniel Dobrowolski, Dr. Andrzej J/edrzejczak from the Institute of Physics in Poland, Warsaw for their guiding and great help in preparing my work to publishing and also to Dr. Monika Arciszewska from the same institute for her useful corrections, for Amit high school for their financial support and also for all people who supported me during my work.

## References

1. V.M. Lyubin, *In Nonsilver Photographic Processes*, Chimia, Leningrad 1984, p. 193
2. M. Klebanov, Proc. SPIE **2426**, 198 (1995)
3. V. Lyubin, Microelectronics **18**, 1.6, 522 (1989)
4. Bulg. Chem. Commun. **26**, (1993)