KFKI-76-4

J. GAZSÓ
J. HAJTÓ
G. ZENTAI

KINETICS OF OPTICAL MEMORY SWITCHING IN CHALCOGENIDE THIN FILMS

Hungarian Academy of Sciences

CENTRAL
RESEARCH
INSTITUTE FOR
PHYSICS

BUDAPEST

KFKI-76-4

KINETICS OF OPTICAL MEMORY SWITCHING IN CHALCOGENIDE THIN FILMS

J. Gazsó, J. Hajtó, G. Zentai

Solid State Physics Division

Central Research Institute for Physics
1525 Budapest P.O.B. 49., Hungary

Submitted to Thin Solid Films

ISBN 963 371 103 7

ABSTRACT

Crystallization and reamorphization of As-Te-Ge chalcogenide thin films exposed to a pulsed laser beam have been investigated and direct information about the change in the speed of crystallization and amorphization has been obtained. The relation between time and minimum power needed for crystallization is presented. Microscopic examination of the diameter shows that laser writing and erasing can be ascribed to the thermally induced phase transition of the material. An estimate based on computer simulation of heat conductivity gives a lower limit of 0.1 μsec for the writing-in process.

АННОТАЦИЯ

Нами были изучены кристаллизация, аморфизация и скорость фазового перехода халькогенидных пленок с составом As-Te-Ge с помощью лазерных импульсов. Нашы были измерены зависимость длительность записи от минимальной мощности лазерового излучения.Електрон-микроскопическое исследование кристаллических точек показало что запись и стирание является результатом термического фазового перехода вещества Длительность записи полученные из уравнения теплопроводности равнялась 0.1 μсек.

KIVONAT

As-Te-Ge összetételü kalkogenid vékonyrétegek lézer impulzusok hatására történő kristályosodását és reamorfizációját tanulmányoztuk és meghatároztuk a fázisátalakulások sebességét. Vizsgáltuk a kristályosodáshoz szükséges minimális lézer teljesitmény és a beirási idő közti összefüggést. A kristályosodott foltok elektronmikroszkópos vizsgálata azt mutatja, hogy a lézeres beirást és törlést a vékonyrétegek hőmérséklet aktiválta fázisátalakulásával lehet magyarázni. A beiró folyamat sebessége a hővezetőképességi modell alapján számolva nem lehet rövidebb mint 0.1 μsec.

1. Introduction

Reversible changes in the reflectivity of Te-based chalcogenide films by laser irradiation have recently been reported /1-5/. It was found that the optical properties were altered by short laser pulses on chalcogenide films using mainly the amorphous or crystalline forms as starting materials. The thermodynamic data of Te-based thin films showed that the heat treated amorphous films contained Te crystals at about 220°C; at higher temperatures of about 260°C, Ge-Te was produced /6-8/. On cooling down the melted sample, two different thermodynamic phases may be obtained depending on the cooling rate and the compositions. However, if the melted material is cooled rapidly to room temperature it solidifies in the amorphous state.

The speed of "photocrystallization" in thin films is of the order of microseconds /9/ according to the speed of the amorphous - crystalline phase transition. The "photo-amorphization" is a faster process than that of the reverse mode /10/ and can take place within nanoseconds at the temperature of the phase transition. To obtain re-amorphized spots at room temperature, the process is controlled by the cooling rate of the material; values of the order of 10^{10} °C/sec have been calculated. A study of the crystallization kinetics has

shown /1/ that it can be reconciled with thermal effects only.

In this paper we summarize our results on laser--writing and erasing in chalcogenide thin films. The investigations on switching time and the data of electron-microscopic examination compared with the results of computer solution are detailed.

2. Sample preparation and experimental technique

Thin films of the chalcogenide alloys were prepared by the co-evaporation of the three elements of As, Te and Ge onto a glass substrate and simultanously onto a carbon collodium cover on a sample grid for electron-microscopic measurements. The film compositions measured by mass-spectrometrial analysis were found to be $Te_{80}Ge_{15}As_5$ and $Te_{88}Ge_6As_6$. Film thicknesses were nominally 210 Å and 670 Å. The morphological changes were photographed with a YEM 100 U transmission electron-microscope. The electron--micrograph and the diffraction pattern of the two films are shown in Fig. 1.

The diffraction pattern of the 210 Å thick film was characteristic for amorphous films but the 670 Å film was in the polycrystalline state. Crystallization takes

place during the thermal treatment of the layer - at about 230°C. This process may occur during the deposition of the film if the sample holder is not cooled. This fact has to be taken into account by the depositing of layers with thicknesses of more than 500 Å.

A modulated He-Ne laser beam / λ = 6328 Å/ was used for writing and erasing /crystallizing and amorphizing/ in amorphous chalcogenide thin films and its light intensity was monitored /Fig. 2/. Simultanously a He-Cd laser beam / λ = 4416 Å/ was threaded through the written spon in order to obtain direct information about the change in the speed of crystallization and amorphization. The change in transmission of the sample was detected by a photomultiplier 14 .

3. Results

Sensitivity dependence

Optical storage media can be classified into two groups 11 depending upon whether the photoresponse involves primarily sensitivity to the exposure energy /photographic media/, or sensitivity to the exposure intensity /threshold materials/. The Te-rich memory alloys generally show the photocrystallization phenomenon which leads to the threshold recording characteristics. Therefore our

first aim was to determine the relation between the laser pulse duration and the minimum power needed for crystallization to set in for the $Te_{88}Ge_6As_6$ thin films.

As Fig. 3 shows, the power - time relation in logarithmic scale is a straight line with a slope of - 1/3 in the /usec region but for higher "t" values as $t > 10^4$ /us the power limit becomes a constant. This constant value gives the minimum power needed for the onset of crystallization at which stage the heat loss and the heating by the laser are just in equilibrium and the temperature is just above the crystallization limit. This minimum power depends on a series of optical and thermal parameters: e.g. reflectivity and adsorptivity of the specimens at the given wavelength, heat capacities and conductivites, film thickness, etc. The failure of the reciprocity law between the pulse length and the exposure intensity involves that our alloy is none of the two extremes. We were unable to carry our measurements under 0.1 /usec because of the power limit of our He-Ne laser, though from heat conductivitiy considerations 0.1 /usec seems to be a lower limit value for successful crystallization /see Discussion/.

Speed of phase changes

The second aim of our investigation was to measure the speed of the amorphous-crystalline and crystalline-

-amorphous phase changes. The results shown in Figs 4a and b were obtained at a laser power of 13 mW.

Figure 4a shows the change in the light intensity of the He-Cd reading laser beam having gone through the written spot. The dotted line represents the form of the crystallizing pulse the length of which is chosen so that crystallization is completed during the light pulse and no changes take place after it. In this case the speed of "writing" is limited by the duration of the amorphous-crystalline phase transition which was shorter than 0.5 μsec. Figure 4b shows the kinetics of amorphization /"erasing"/ by the same laser power /13 mW/. The melting of the material needs higher energy than does crystallization so we used a longer pulse. The duration of amorphization and crystallization processes were approximately equal at a given laser power. These results are not inconsistent with the results of Gutfeld and Chaudhari [10] : the amorphization process may indeed be more rapid than the crystallization if the exposure intensities are not restricted.

Repeated testing

Writing-erasing cycles with fixed laser power /13 mW/ were carried out on the same spot, which was switched 150 times without any demage. Figure 5 shows the photo-

multiplier signals, plotted by an X-Y recorder. The time scaling is much greater, so the switching pulses themselves cannot be detected, only the changes in transmittivity caused by them. The time needed for crystallization is constant during cycles, but the pulse length, i.e. /energy/ needed for reamorphization increased somewhat during switchings /0.54-0.6 /usec/. This is experimental proof of the fact that the energy needed for reamorphization depends on the degree of crystallization 1 .

There is a sharp limiting value of 0.61 /usec for amorphizing pulses /at 13 mW power/: shorter pulses are not capable of transforming the crystalline spot into the amorphous state totally, but they do increase the remaining part in the crystalline state.

Electron microscopic examination

Electron-microscopic examination was carried out to determine the morphological changes during the writing - erasing cycles.

Pulses of 0.54-0.6 /usec from the He-Ne gas laser were used in the films of 670 Å thickness /polycrystalline ad deposited/. Figure 6a shows the transmission electron micrograph of the yielded structure. As can be

observed, the central region with the diameter of about 0.5 μ is perfectly amorphous; here the material was melted /$T > 375^{\circ}C$/. This central region is surrounded by a halo region to the diameter of 1 μ. Here the polycrystalline structure is conserved /$225^{\circ}C < T < 375^{\circ}C$/, but the crystallites are rough. In the light-microscopic observations the amorphous spots are more transparent, and the reflectivity increases with the size of the crystallites. In Figure 6b the same spot is depicted in the "erased" state: in the place of the central amorphous region recrystallization has occurred under the heating influence of the focused electron beam of the electron microscope.

Films deposited from the vapour on room temperature substrates contain defects in high concentration and the numbers of these defects are greatly reduced during high temperature annealing. The most dense films are those which have been annealed at the highest temperature. This effect can be demonstrated by scanning electron microscope observations. In Fig. 7a, the central, hottest region of the laser exposed area is seen to be more concave. The structure corresponds to that shown in Fig. 6b i.e. the whole film is crystalline but the central part is the most dense. In the amorphized state the surface of the concavity has been smoothed /Figs 7b and 6a, respectively/. The data of the X-ray microanalyser showed no change in

the composition of the laser irradiated areas; it is true, however, that the resolution of this equipment was not better than 4 /u. On applying too intense pulses, the material melts, evaporates, and flows out /Fig. 7c/.

Temperature behaviour

The radial and temporal temperature profiles of the laser induced areas can be obtained as a first approximation by solving the following differential equation of heat conduction 15

$$c_p \rho h \frac{\partial T}{\partial t} = Q(r,t) + \lambda h \Delta T \qquad /1/$$

where: C_p = specific heat, ρ = density, λ = thermal conductivity, h = thickness of the film, Q = laser flux density whose form is assumed to be Gaussian:

$$Q = Q_0 \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{1}{2}\left(\frac{r}{\sigma}\right)^2} \qquad /2/$$

This analysis ignores the differences in thermal conductivity, reflectivity and absorptivity between the crystalline and the amorphous regions. The problematic effect of latent heat 16 is neglected, too.

From the distribution /2/ it follows that equation /1/ can be used only when the thickness of the film is

many times smaller than the diameter of the laser induced areas. This calculation is for the case of chalcogenide films on a thin carbon collodium layer: heat loss is taken into account only at the circular boundary of the spot. Taking the values h = 0.067/u, d = 1-3/u, c_p = 0.09 cal/gr ^{o}C, ρ = 5.61 gr/cm^3, λ = 1 kcal/m^{o}Ch, we found the following results:

In the case of the 0.4/usec pulse the temperature of the illuminated area /2.8/u diameter/ reaches the crystallization temperature range /T_x = 225^{o}C-375^{o}C/.

Using a 0.6/usec pulse for reamorphization the temperature in the central region /0.5/u diameter/ according to the Gaussian form of the laser flux density reaches the melting temperatures of the material /T_m = 375^{o}C/.

We found the cooling rate values predicted by the equation of heat conduction to be of the order of 600^{o}C/usec. This rate was sufficiently rapid for the melted material to remain in the disordered /amorphous/ state.

A summary of our results is shown in Table I.

Laser power mW	Pulse duration /us	Diameter of crystalline spots / u/		Diameter of amorphous spots	
		Electron microscopic observation	From equation of heat conduction	Electron microscopic observation	From equation of heat conduction
13.1	0.3	2.6	2.8	-	-
13.1	0.4	2.75	3.0	-	-
13.1	0.52	3.1	3.3	0.4	0.5
13.1	0.6	3.2	3.45	0.5	0.55

The diameter of amorphous spots are 0.4-0.55/u, but during amorphization a crystallization also takes place around the amorphous spots. The diameter of the crystalline region limits the packing density of the material: an order of 10^7 bit/cm^2 can be reached.

4. Discussion

In contrast to the As_2S_3, As_2Se_3 and related alloys, where photostructural changes appear to be the result of a non-equilibrium distribution of trapped charges created by illumination [11], the study of the phase changes in the Te-rich thin films shows that the effects in them may be purely thermal in origin. The reciprocity failure seems to be attributed to the sensitivity dependence on the exposure intensity. In the limit of exceedingly short

/5 to 100 nsec/ pulses the sensitivity is stated to be higher /1, 10/; conversely, for long pulse exposures, e.g. 10^{-3} to 10^{-5} sec the sensitivity may be 10 to 10^3 times smaller 9 .

Since there are no generally accepted models or theories of the glass transformation, the following question may arise: does crystallization and revitrification occur via a process glass ↔ liquid ↔ crystal or directly glass ↔ crystal? 12 . Vitrification need not always involve thermodynamic melting as Herd and Chaudhari 13 demonstrated for electron beam exposure of Se at -100°C. In our case, however, for repeated testing on the same spot, there was a narrow range for the right vitrification pulse length: /0.605±0.005/ μsec at 13 mW laser power /Fig. 6/. Longer pulses caused the evaporation of the material /Fig. 5/ so it seems to be certain that amorphizing laser pulses do cause melting /Fig. 8c/.

It follows from the curves of the computer solutions of the heat conductivity that the decay time constant characteristic for the investigated spots with the given sample parameters is of the order of some hundreds of nanoseconds. /In our estimate the loss by thermal radiation which diminishes the decay constant at elevated temperatures was not taken into account./ Crystallization falls

to zero near to the melting point, and it should have its maximal values within the temperature range of 225°C to 325°C /Fig. 8/. Cooling the material in the central region of the spot, i.e. in the case of short ending of the vitrification pulses, the temperature crosses this critical interval during approximately 0.1 /usec /Fig. 8/. It should, however, be mentioned with regard to this estimate that for shorter pulses the attempt to write in may not results in perfect crystallization /at whatever high laser intensities/ due to the thermal parameters of our chalcogenide thin films.

REFERENCES

1 K.Weiser, R.I.Gambino, I.A.Reinhold: Appl.Phys. Letters 22 /1973/ 48

2 J.Feinleib, J.P.de Neufville, S.C.Moss., S.R.Ovshinsky: Appl.Phys.Letters 18 /1971/ 254/

3 M.Terao, H.Yamamoto, S.Asai, E.Maruyama: Prod. 3rd Conf. Solid State Devices, Tokyo /1971/ 68

4 S.Asai and E.Maruyama: Japan Soc.Appl.Phys. Tokyo /1970/ 172

5 J.Feinleib, S.Iwasa, S.C.Moss, J.P. de Neufville, S.R.Ovshinsky: J.Non-Cryst. Solids 8-10 /1972/ 909

6 H.Fritzsche, S.R.Ovshinsky: J.Non-Cryst. Solids 2 /1970/ 147

7 D.L.Eaton: J.Am.Ceram.Soc. 47 /1964/ 554

8 A.D.Pearson, in: Advances in Glass Technology, Plenum Press, New York /1963/ 145

9 A.Hamada, T.Kurosu, M.Saito, M.Kikuchi: Appl.Phys. Letters 20 /1972/ 9

10 R.I.von Gutfeld, P.Chaudhari: J.Appl.Phys. 43 /1972/ 4688

11 J.P. de Neufville, in: Proc. 5th Int.Conf.Amorph. Liquid Semic. /1973/ 1351

12 A.E.Owen, in: Electr.Struct.Prop. of Amorph.Semicond. /ed. P.G.LeComber and J.Mort/ Academic Press, London and New York /1973/ 161

13 S.Herd, P.Chaudhari: J.Appl.Phys. 44 /1973/ 102

14 G.Zentai: Proc. "Amorph.Semicond.'74" /Reinhardsbrunn, GDR/ 441

15 J.Hajtó, G.Ács: Proc. "Amorph.Semicond.'74" /Reinhardsbrunn, GDR/ 437

16 R.J. von Gutfeld: Appl.Phys.Lett. 22 /1973/ 257

FIGURE LEGENDS

Fig. 1. Electron micrograph and the diffraction pattern of evaporated a./ 210 Å and b./ 670 Å thick films

Fig. 2. Measuring arrangement

Fig. 3. Minimum power vs. pulse length

Fig. 4. Kinetics of phase changes
a/ amorphous - crystalline; b/ crystalline - amorphous

Fig. 5. Repeated writing - erasing test on one spot

Fig. 6. Transmission electron micrographs of
a/ an amorphous spot in starting polycrystalline $Te_{88}Ge_6As_6$ film
b/ the recrystallized state via slow electron beam heating
c/ the crystallized spot exposure to laser beam

Fig. 7. Scanning electron micrographs of
a/ crystallized spot
b/ reamorphized spot
c/ burned-out spot

Fig. 8. Temporal temperature behaviour of the chalcogenide film using a simple radial heat flow model for computer simulation
a/ slow crystallization pulse
b/ rapid crystallization pulse
c/ amorphizing pulse

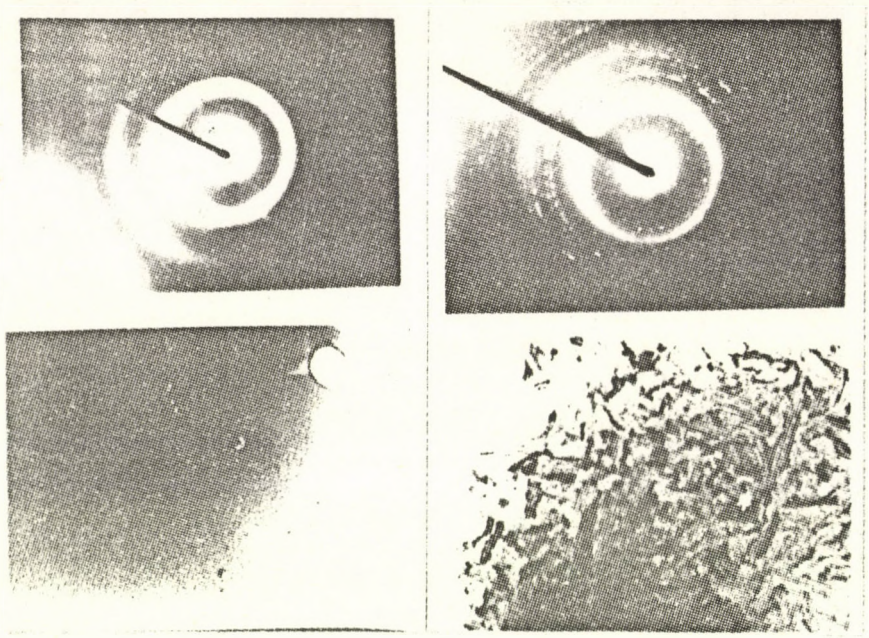


Fig. 1

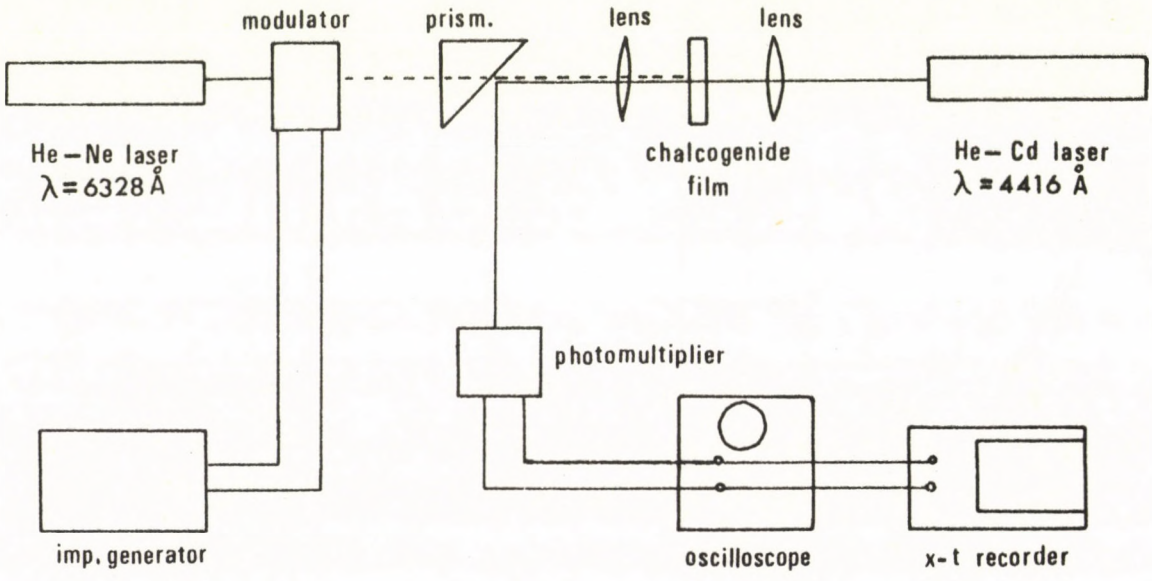

modulator
prism.
lens
lens
He – Ne laser
λ = 6328 Å
chalcogenide
film
He – Cd laser
λ = 4416 Å
photomultiplier
imp. generator
oscilloscope
x-t recorder

Fig. 2

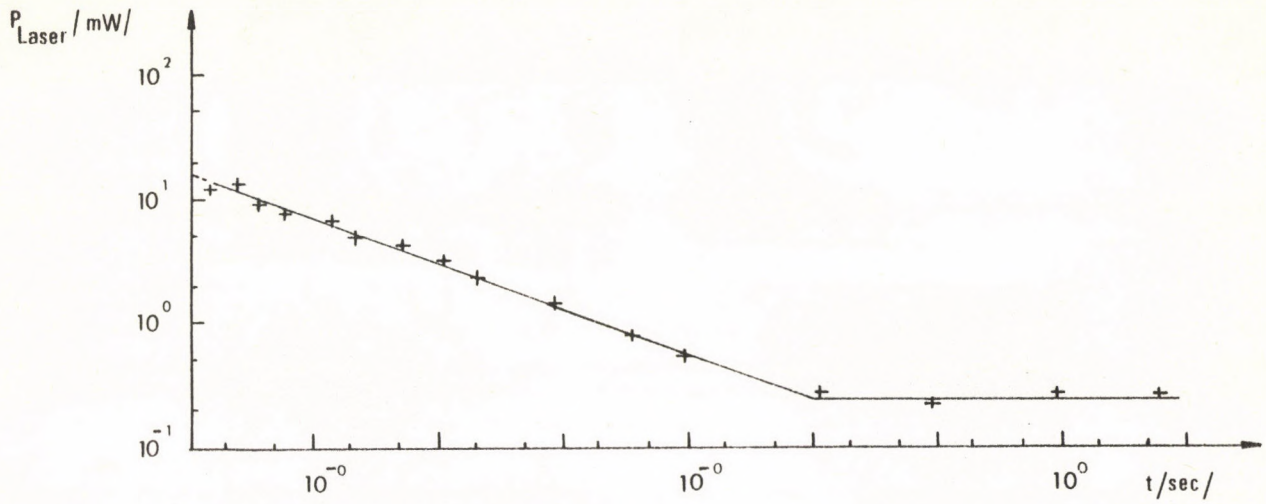

P Laser / mW/
10^2
10^1
10^0
10^-1
10^-0
10^-0
10^0
t/sec/

Fig. 3

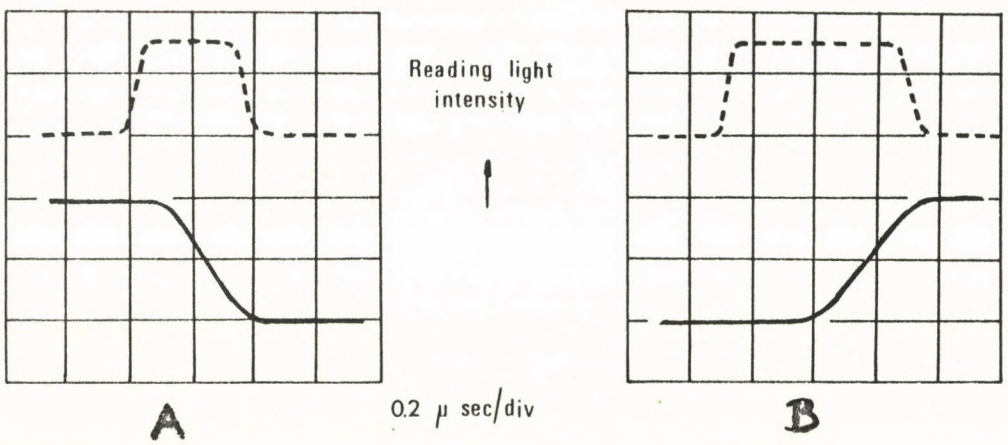

Reading light intensity
A
0.2 μ sec/div
B

Fig. 4

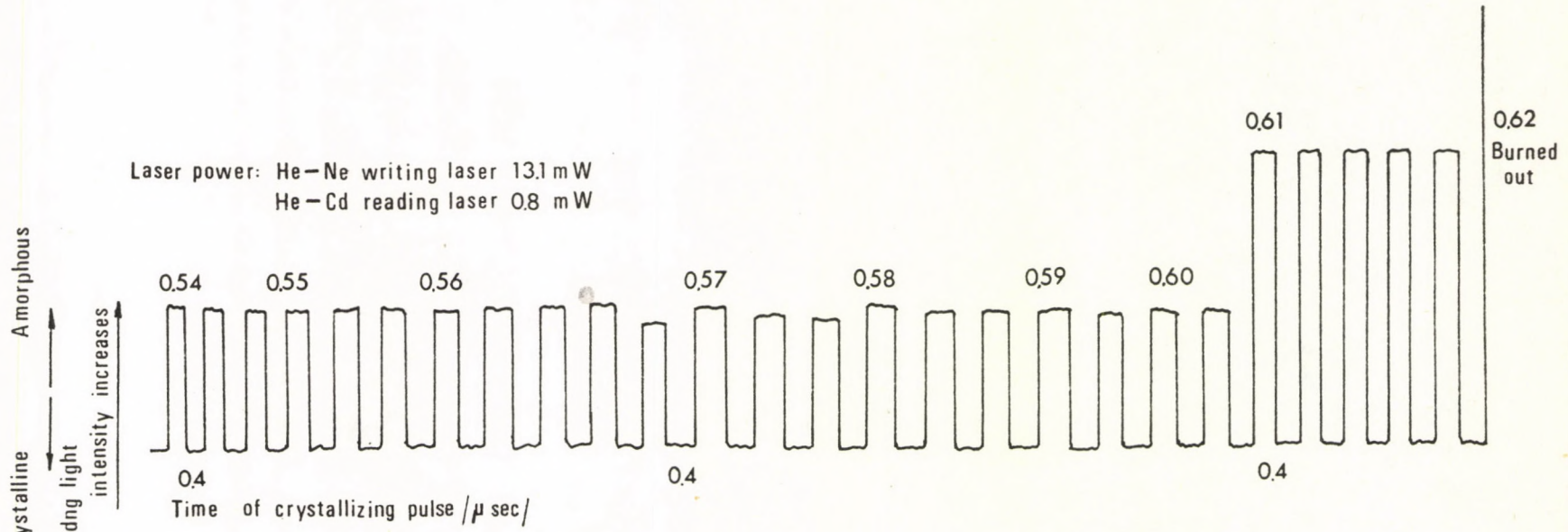

Laser power: He–Ne writing laser 13.1 mW
He–Cd reading laser 0.8 mW
Crystalline
Amorphous
readng light intensity increases
0.54
0.55
0.56
0.57
0.58
0.59
0.60
0.61
0.62
Burned out
0.4
0.4
0.4
Time of crystallizing pulse /μ sec/

Fig. 5

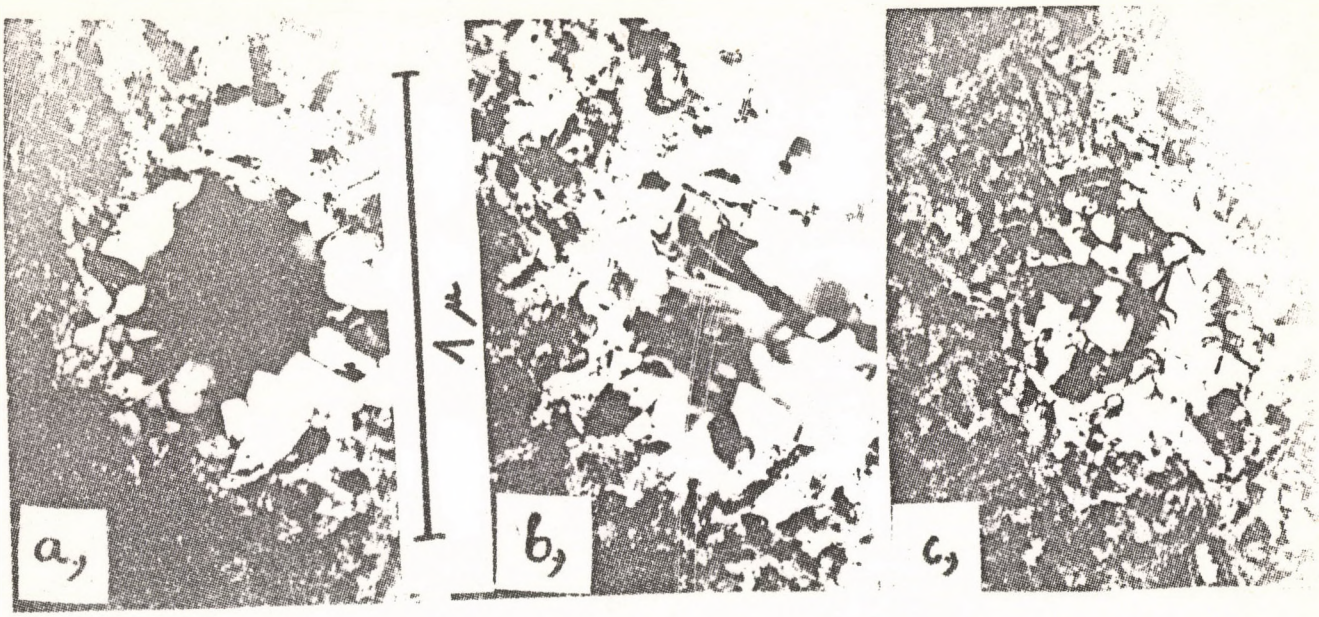


Fig. 6

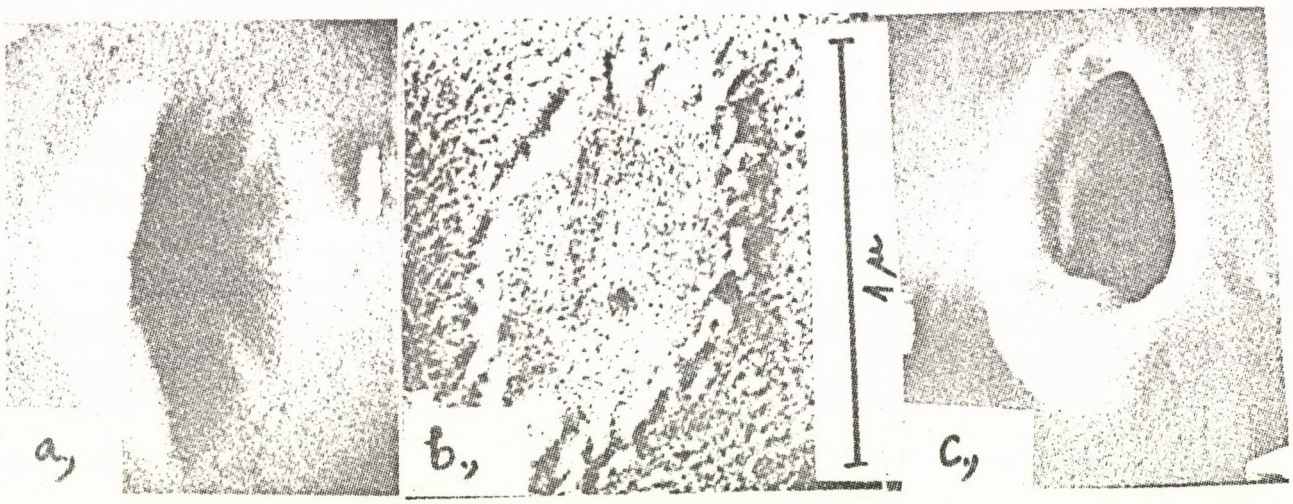


Fig. 7

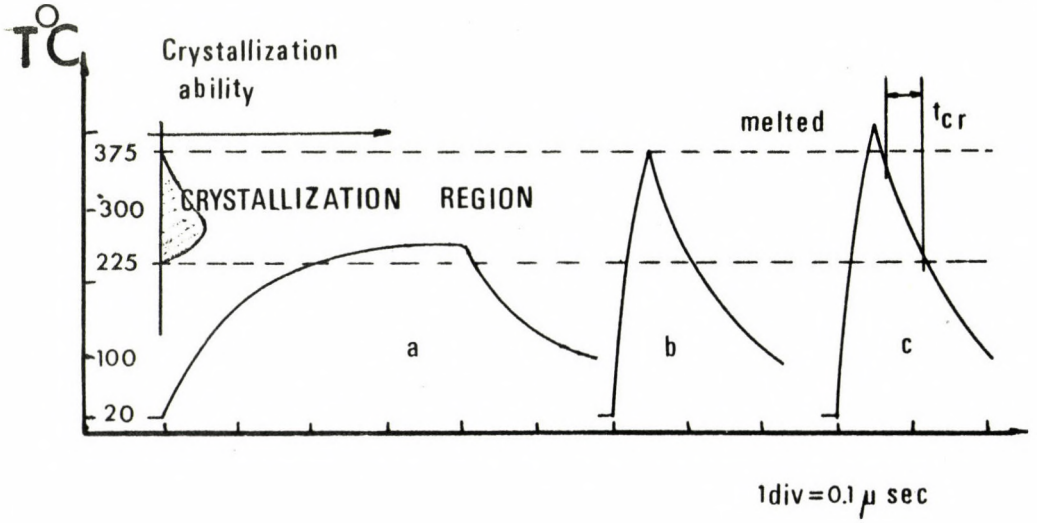
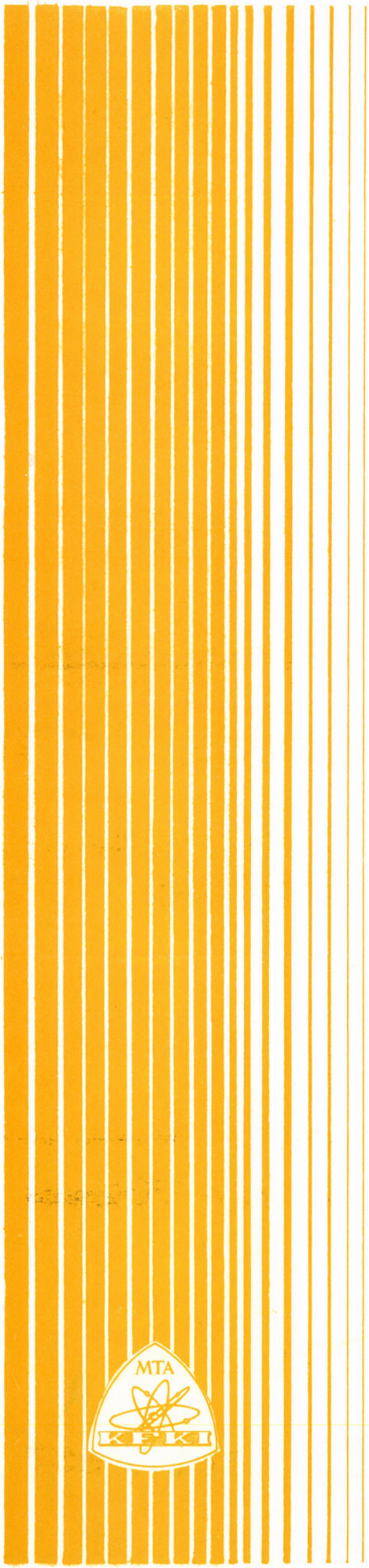

T°C
Crystallization ability
375
300
225
100
20
CRYSTALLIZATION REGION
a
b
c
melted
tcr
1div=0.1 μ sec

Fig. 8



Kiadja a Központi Fizikai Kutató Intézet
Felelős kiadó: Kósa Somogyi István, a KFKI Szilárdtestkutatási Tudományos Tanácsának szekcióelnöke
Szakmai lektor: Grüner György
Nyelvi lektor : H. Shenker
Példányszám: 290 Törzsszám: 76-20
Készült a KFKI sokszorosító üzemében
Budapest, 1976. január hó