Kodak Phase-Change Media For Optical Tape Applications

Yuan-sheng Tyan, Donald R. Preuss, George R. Olin, Fridrich Vazan, Kee-chuan Pan, and Pranab. K. Raychaudhuri

Electronic Imaging Storage Research Laboratories, Eastman Kodak Company, Rochester, New York 14650-2017

INTRODUCTION

The amount of data generated and handled in our lives is increasing at an astonishing rate. The need to store, manage, and in some cases archive this ever-increasing amount of data has become a challenge. Advances in conventional methods of data storage such as paper, microfilm, magnetic tape, and magnetic disk will solve some of these problems, but it has become increasingly apparent that other solutions are desirable. One such possible solution is optical tape. It offers the potential of being a high-capacity, low-cost, and low-maintenance technology for not only storing but at the same time archiving data. The introduction of CREO's optical tape recorder[1] demonstrated the technical feasibility of optical tape systems. Advances in hardware and media in costs and performance are needed to make this technology widely accepted in the future.

The SbInSn phase-change write-once optical medium developed by Eastman Kodak Company is particularly suitable for development into the next generation optical tape media. Its performance for optical recording has already been demonstrated in some of the highest performance optical disk systems (the 10.2 GB per disk 14" Kodak Optical Disk System 6800 and the 20 GB per side Ar laser based GE Juke Box system at NASA Huntsville). Some of the key performance features are:

- Good writing sensitivity. At 0.3 nJ/mm^2, it is among the most sensitive optical media. Since high-capacity storage systems need high data rate, and the rate of optical recording is in most cases limited by available laser power, high recording sensitivity is desirable.

- Good signal-to-noise ratio. Since the rate of read back in well-designed systems is limited by signal-to-noise ratio, this medium will allow high rate readback.

- Wide wavelength response. Being a metallic alloy, the SbInSn alloy has optical properties that are only weakly dependent on wavelength. The same alloy used for 830 nm recording in the Kodak 6800 system is used for the GE Juke Box using 488 nm Ar laser recording. The wavelength dependence will increase somewhat if a scratch-rsistant overcoat is used. It is still possible, however, that the same formulation designed for the IR lasers today will be compatible with the shorter wavelength lasers of the future to further increase the recording capacity.

- Good resolution. The phase-change recording process is based on transformation of atomic structure and not on macroscopic materials flow. The recording principle is simple and is based purely on the thermal crystallization effect. Any part of the thin-film that is heated above the crystallization temperature is crystallized, and the other parts stay amorphous. The sharpness of the transition is determined by the temperature profile produced by the heating laser beam as well as the dependence of crystallization rate on temperature. The SbInSn material has low thermal conductivity, which results in sharp temperature profiles. It also has an unusually large temperature dependence of its crystallization rate. These two effects lead to

extremely sharp transitions. Experimentally we have demonstrated that the transition width is only on the order of nanometers. The mark size and hence the recording density depends only on how small a spot we can heat with the write beam. It will not be limited by media properties.

In addition, this storage medium also appears to be exceptionally stable. This paper presents some of the studies on the fundamental stability of the medium to demonstrate its suitability as an archival medium.

THE SbInSn MEDIUM

The SbInSn medium is an alloy thin-film prepared by DC-magnetron sputtering using an alloy target of the same composition. As deposited, the film shows no ordering under x-ray or E-beam diffraction and is considered amorphous. Since the amorphous structure is not thermodynamically stable, the film will convert eventually into a crystalline phase. When this happens, the optical properties will change. The indices of the amorphous phase at 830 nm are about 5.07 + 2.62i and those of the crystalline phase 3.64 + 5.52i. The reflectivity of the alloy will, therefore, increase as a result of crystallization (Fig. 1). The crystallization process can be accelerated by heating. The optical recording process uses a focused laser beam to heat selected areas on the thin-film and record information in the form of higher reflectivity crystalline marks. Figure 2 shows an optical micrograph of some laser recorded marks. Figure 3 shows laser- recorded marks under TEM where the featureless amorphous background and the crystalline marks are clearly visible.

Since the recording process involves only a solid-state crystallization process, the construction of the recording element is flexible. In the Kodak 6800 system, the 14" disk has an aluminum substrate with both surfaces coated with a surface-smoothing polymer layer. The phase-change layer is coated on top of the surface-smoothing layer. A thin polycarbonate membrane is then suspended about 0.35 mm over the phase-change layer to provide dust defocusing. The disk thus has an air-sandwich structure with first surface recording. The 14" disks supplied to NASA, on the other hand, utilize glass substrates. The phase-change layers are coated directly onto the substrates. Two pieces of coated substrate are then laminated together, with phase-change layers facing each other, using adhesives. These disks are thus in a solid-sandwich structure for through-substrate recording. To construct an optical tape, it is envisioned that the phase-change layer will be coated on a suitable thin-support and that a scratch-resistant layer will be applied over the surface of the phase-change layer. The scratch-resistant layer is used mostly to prevent defects being generated because of the tape-to-tape contact during the wind-unwind operations. In a well-designed optical tape recorder, there should not be the kind of head-media contacts as experienced in magnetic recorders.

STABILITY STUDIES

To evaluate the stability of the medium our approach is to first make a list of conceivable degradation mechanisms. We then designed and performed experiments to try to quantify their rates. For a phase-change medium, the following are the most probable mechanisms:

- spontaneous crystallization of the amorphous phase
- extended mark growth
- growth of the subthreshold heated region
- restructuring of the amorphous phase
- restructuring of the crystalline phase
- corrosion in high temperature and humidity
- oxidation

We will examine these mechanisms in the following sections.

SPONTANEOUS CRYSTALLIZATION OF THE AMORPHOUS PHASE

The principle of phase-change recording is based on the strong temperature dependence of the crystallization rate. For use as an optical recording medium, a phase-change material needs to have a low rate of crystallization at around room temperature so that the medium can be kept for years without spontaneous crystallization. It is also necessary that the rate will increase significantly at elevated temperatures so that during the recording process, the material can be heated by the laser beam to complete the crystallization process in a few nanoseconds. The temperature dependence of the kinetics of the crystallization process can be studied by studying the thermal crystallization process. A sample is placed on a hot plate and heated at a constant temperature ramp rate while its optical reflectance is continuously monitored. At a certain temperature the sample will crystallize and an abrupt increase in reflectance will be observed. This temperature is called the crystallization temperature and is the temperature at which the rate of crystallization matches the rate of heating. When the temperature ramp rate is increased, the crystallization temperature will also increase. By studying the dependence of crystallization temperature on heating rate, the dependence of crystallization rate on temperature can be deduced.

Figure 4 shows the results of such a study. Here $\log(\beta/T^2)$, where β is the heating rate, is plotted against $1/T$. A straight line as indicated in the figure suggests a thermally activated behavior where the slope of the line is proportional to the activation energy. The actual data can only be collected over a very limited temperature range (at about 170°C) where the experiments lasted from a few minutes to a few days. It is seen that the temperature dependence is exceedingly strong. A three-orders-of-magnitude increase in the heating rate only results in an increase of crystalline temperature by a mere 14°C. The calculated activation energy is almost 200 kcal/mole, or over 8 eV. The origin of such an exceptionally high activation energy is not understood at the present time. From these data, it is possible to estimate the amount of time needed to complete 50% crystallization as a function of temperature (Fig. 5). If the observed temperature dependence can be extrapolated to lower temperatures, then the time for 50% crystallization at 50°C is predicted to be more than 10^{30} years, which is longer than the predicted lifetime of the universe. Obviously something else will happen before this, but the data do indicate that the stability of the amorphous phase by itself should not be of a practical concern.

If the temperature dependence can be extrapolated to higher temperatures, then it is predicted that the material needs only to be heated to about 230°C to have the crystallization completed in 10^{-10} seconds, a rate required for high-speed recording. This is to be compared with ablative type optical media that have to be heated to much higher temperatures in order to achieve melting or vaporization of the materials. The small heating requirement is the main reason for the superior writing sensitivity of the SbInSn medium.

EXTENDED CRYSTALLINE MARK GROWTH

Crystallization process in SbInSn proceeds via the normal nucleation and growth process. It is possible, therefore, that even though the amorphous phase is stable by itself, growth of the recorded crystalline marks will destroy the data before the spontaneous crystallization of the amorphous phase. Figure 6 shows the TEM micrographs of a laser-recorded mark before and after heating for an extended period of time at high temperatures. Indeed irregular growth of the crystalline boundary is observed even though the amorphous background remains unchanged. We call this the extended mark growth to distinguish it from the uniform mark growth to be discussed later.

To study the kinetics of the extended mark growth, a series of samples with prerecorded marks were heated at various temperatures for extended periods. At selected time intervals, microscopic examinations of the prerecorded marks were performed to determine the extent of mark growth. The results indicated that the growth rate is essentially constant with time and it increases exponentially with temperature. Figure 7 shows a plot of the time needed for a 3

mm increase of mark diameter as a function of temperature. It also shows the estimated time needed for 100 nm growth. We labeled the latter the end of life because an irregular growth of such an extent would increase jitter significantly and an appreciable degradation in phase-margin in a pulse-length-modulated recording system would have resulted at this stage. For pulse-position-modulation system or fixed-bit-cell recording system this estimate could be overly conservative.

The data in Fig. 7 indicated that the predicted lifetime based on this conservative criterion is over a thousand years at 50°C. Extended mark growth will not, therefore, limit the lifetime of this medium.

GROWTH OF THE SUB-THRESHOLD HEATED REGION

In addition to the extended mark growth that is observed when the samples are heated to higher temperatures, we also observed another kind of mark growth at relatively lower temperatures. In this case there seems to be a uniform growth front. The marks will become larger with time but no increase in jitter is observed as a result of this growth. The growth has a logarithmic dependence on time. It is fast initially, but slows down significantly afterwards and hence is self-limiting. It also has a temperature dependence. Figure 8 shows the observed rate of change at various temperatures. For example, at 80°C the mark will grow in diameter by a total of 13 nm after a day, but it is only predicted to grow by 26 nm after 300 years.

Evidence suggests that this growth is caused by a subthreshold heating effect. The laser spot used for optical recording has a Gaussian-like intensity profile that generates a Gaussian-like temperature profile in the material. Within a radius near the center, $r < r_c$, the material is heated to a high enough temperature that it becomes crystallized to form a written spot. Just outside the transformed region the material has not crystallized, but it has received substantial heating from the writing laser beam that apparently has caused changes in its properties. It is the growth into this region that is observed when the marks are aged.

Since the growth is predictable and limited, it is not a lifetime-limiting effect. Rather, proper budget in the phase-marging has to be allowed to account for this effect if PWM recording scheme is used. For PPM or fixed-bit-cell recording the impact would be even less.

RESTRUCTURING OF THE AMORPHOUS PHASE

The as-deposited films are in a vapor quenched high free-energy state. The free energy of the films can be reduced by local rearrangement of the atoms without actually crystallizing the films. This effect has been documented, for example, for magneto-optic thin-films.[2] In the MO films, the restructuring causes a change in the magnetic properties. In the SbInSn thin-films, the restructuring reduces the writing sensitivity. The observed reduction in sensitivity again has a logarithmic time dependence and a slight temperature dependence. Figure 9 shows the observed rate of recording power increase at various temperatures. At 60°C an about 10% drop in writing sensitivity is expected over the first year of media life. Since most recorders utilize write calibration strategies, this effect will not affect the lifetime of the media.

RESTRUCTURING OF THE CRYSTALLINE PHASE

In high-rate optical recording processes the total laser exposure time at a given spot on the media is on the order of nanoseconds. Such a small amount of time is usually insufficient for the materials to reach thermal equilibrium. As a result, metastable crystalline phases are obtained. In the case of SbInSn alloy, the laser recording process results in a NaCl-like cubic crystalline structure. The equilibrium state, however, is expected to be a mixture of several crystalline phases. Upon aging a gradual transformation of the laser-written marks into more stable crystalline phases has been observed. Associated with the phase transformation is a slight decrease in the reflectance of the crystalline marks and hence the recording contrast or

the readback signal (the carrier). Figure 10 shows that the change of reflectance depends logarithmically on time and is faster at higher temperatures. Figure 11 shows the resulting degradation in carrier signal at various temperatures. At 60°C, for example, we observed a 1.2 dB degradation after one year. From the data in the figure, we predict a total of 1.5 dB degradation after three hundred years.

CORROSION AT HIGH TEMPERATURE AND HUMIDITY

The SbInSn thin films are exceptional in their corrosion resistance in high temperature and high humidity environments. Incubation of bare films without any protection layer at 70°C, 70% RH for over two years has resulted in no observable corrosion. The rate of corrosion cannot, therefore, be easily quantified. In practical products where an overcoat protection is likely to be used the corrosion rate should be further slowed. It is judged, therefore, that corrosion degradation of these films should not be a concern.

Figure 12 is a TEM micrograph of an SbInSn thin-film that had been incubated for over 4000 hours at 70°C, 70% RH. The film was coated on an injection-molded polycarbonate substrate and recorded with the laser-written marks shown in the picture. The incubation was carried out with the SbInSn film directly exposed to the environment. After the incubation, the polycarbonate substrate was dissolved in a solvent so that the SbInSn thin-film could be mounted on a copper grid for the TEM observation. This abusive sample preparation procedure caused the cracks and stains in the picture. There is, however, no sign of corrosion, nor the crystallization of the amorphous region, nor the extended growth of the prerecorded marks. These results are consistent with the predictions as noted in previous sections.

OXIDATION

The corrosion resistance of the film is believed to be a result of self-passivation: the oxidation process resulted in the growth of a native oxide film that protects the films from further oxidation. This mechanism is commonly observed among most corrosion-resistant metals or alloys. For thin-films, however, a concern is whether the passivating oxide layer will reach a thickness that will affect the performance of the films.

Since the passivating layer is most likely a transparent oxide, one easy way to monitor the thickness of the oxide layer is to monitor the optical density of the thin-film, which gives a good representation of the unoxidized alloy film. Figure 13 shows a plot of the optical density of a 48-nm-thick thin-film heated at different temperatures in air as a function of time. The optical density again has a logarithmic dependence on time, and the temperature dependence appears to be small. The projected oxide thickness after 300 years is less than 5 nm even at high temperatures. In a disk or tape construction, although the maximum change in reflectance between the amorphous and the crystalline phases is observed at about 80 nm film thickness, the actual recording performance is rather constant within a 15% thickness range. Thus a 5 nm decrease in phase-change layer thickness due to oxidation is not expected to have much impact on the recording performance. The long-term incubation studies have confirmed this prediction.

14" DISK DATA

Although all the fundamental studies mentioned above suggest that the SbInSn alloy is a very stable recording medium, real-life confirmation is still necessary. We have subjected many 14" disks to various testing environments, and so far have not had any indications that the projections based on these studies are incorrect. Figure 14 shows the results of extended incubation of several disks at 70°C, 90% RH. It shows virtually no change in uncorrected error rate over the 84-day incubation period.

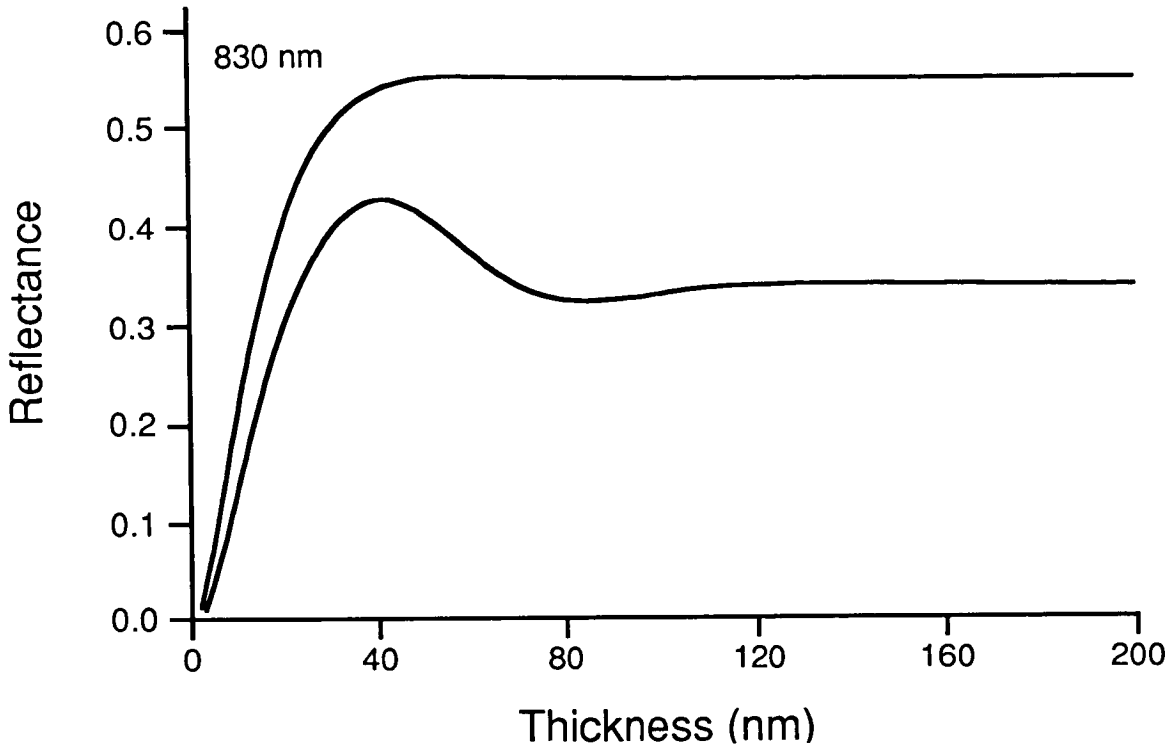
SUMMARY

Extensive degradation mechanism studies suggest that the SbInSn phase-change alloy thin-film is very stable and it will not be the lifetime-limiting factor in any disk or tape medium construction. This superior stability as well as the many virtues listed in the Introduction section makes this alloy an ideal candidate for optical tape applications. Extensive efforts are underway at Eastman Kodak Company to promote optical tape technology based on this material.

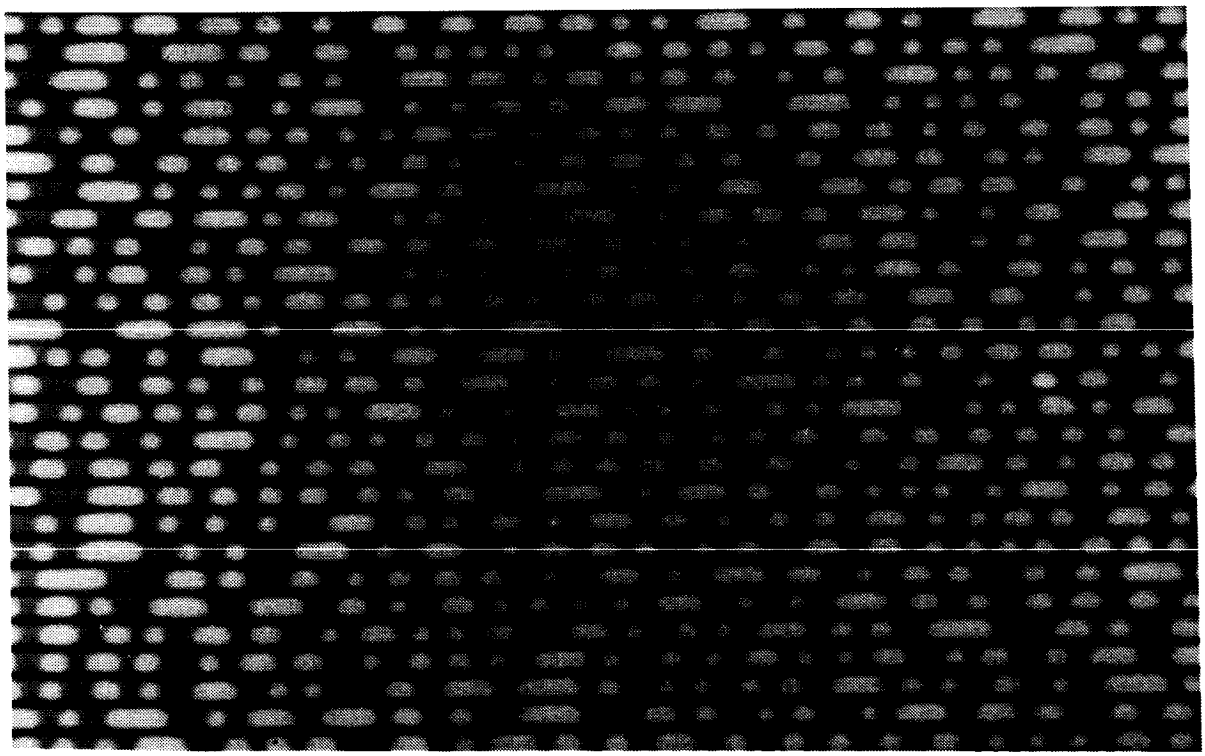
REFERENCES

1. D. Gelbart, Optical Data Storage, SPIE Vol. 1316, p.65 (1990).

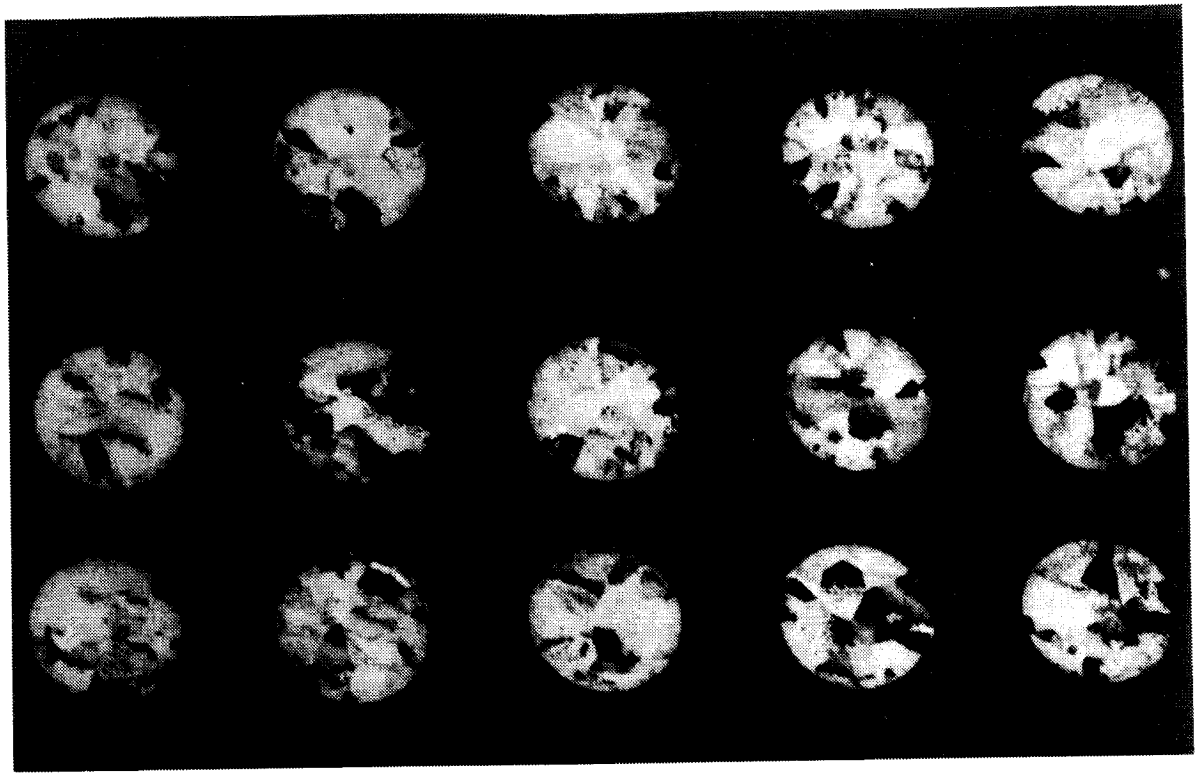
2. N. Ogihara, K. Shimazaki, Y. Yamada, M. Yoshihiro, A. Gotoh, H. Fujiwara, F. Kirino, and N. Ohta, Jpn. J. Appl. Phys., V. 28 (1989), Supplement 28-3, pp 61-66.



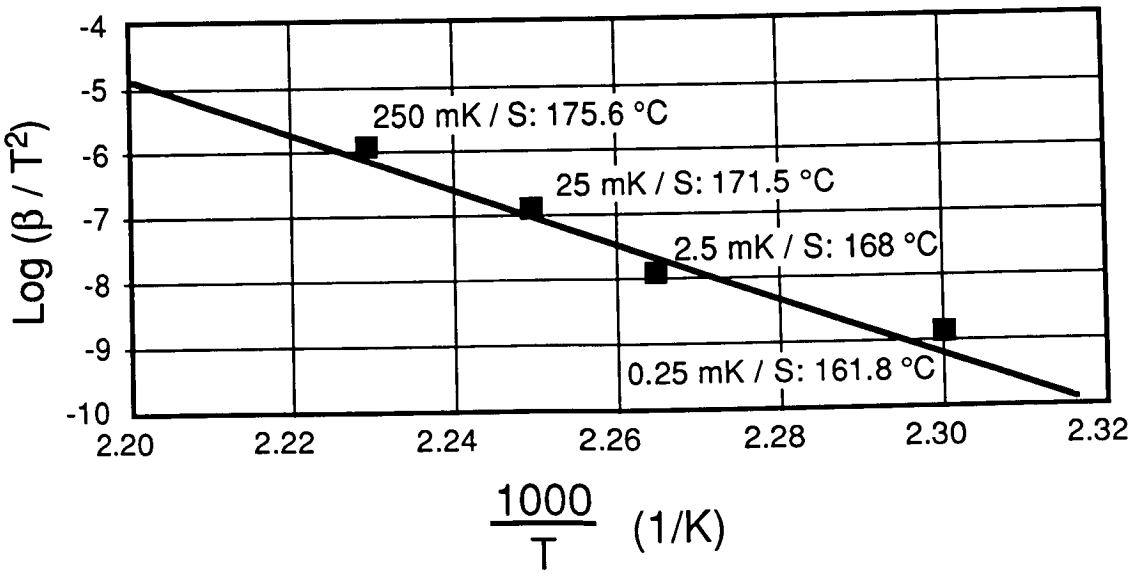
1. **Calculated reflectivity of an SbInSn thin-film for both amorphous and crystalline states as a function of film thickness.**



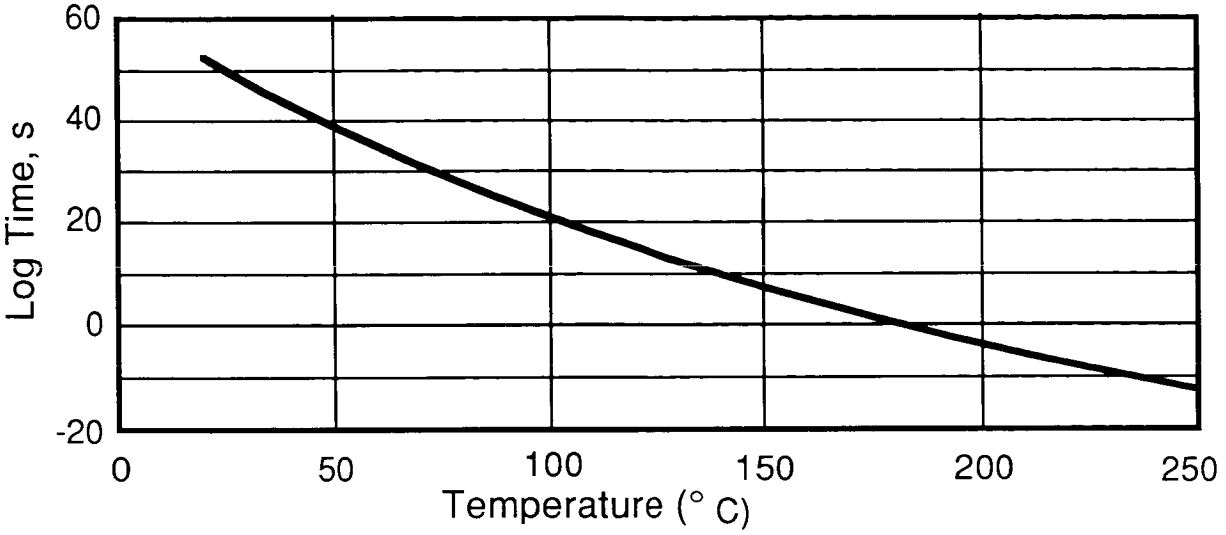
2. **Photomicrograph of some laser-recorded marks in an SbInSn thin-film. (Bright field reflection; the white features are recorded marks. The groove width is 1.6 mm)**



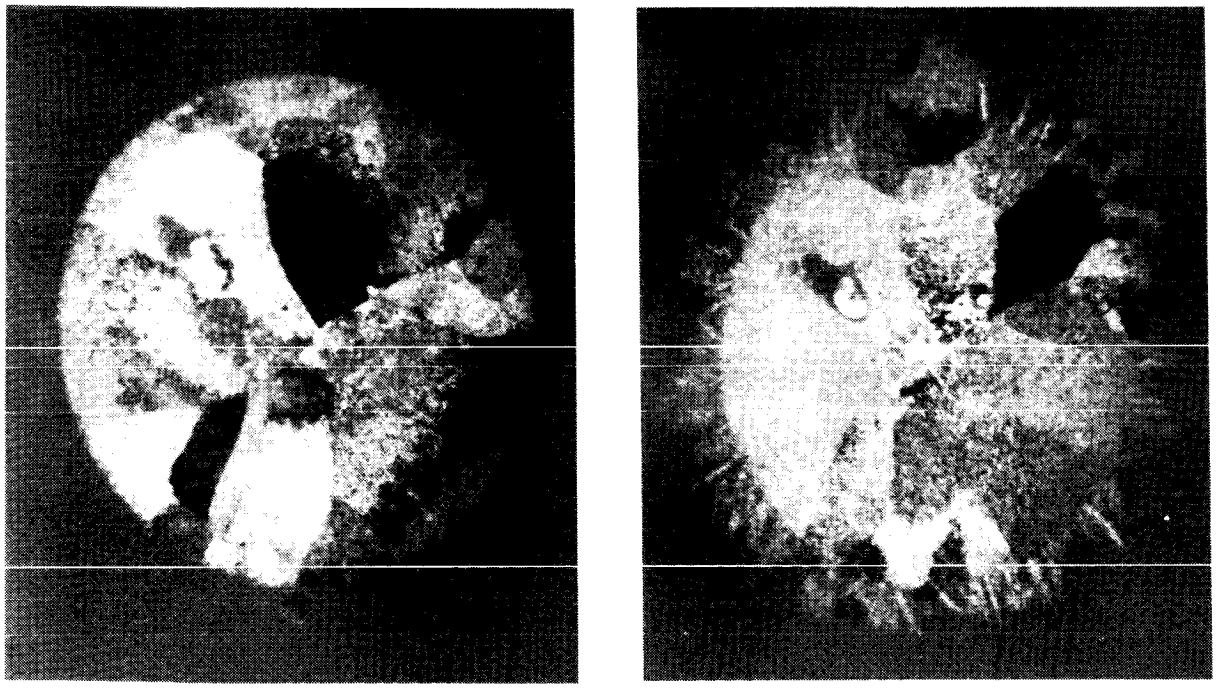
3. **TEM micrograph of some laser-recorded marks. Structure within the marks is due to diffraction of electron beam by crystallites of different orientations.**



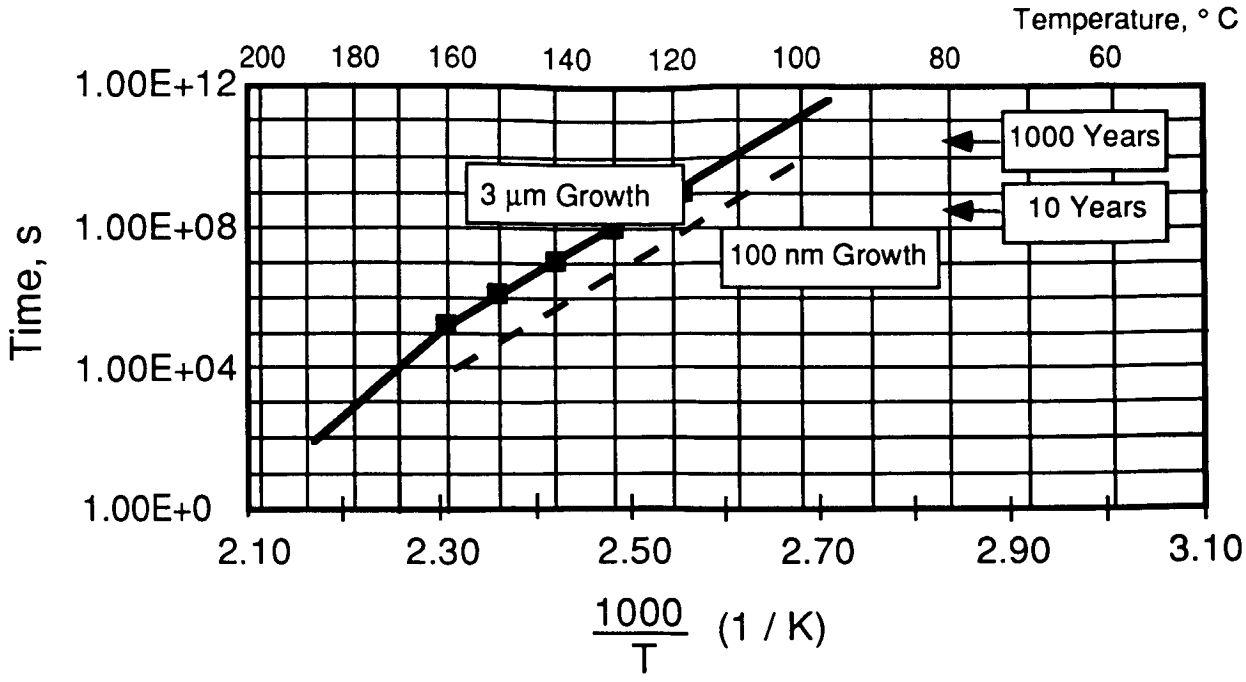
4. **The dependence of measured crystallization temperature on heating rate. The linear dependence indicates a thermally activated behavior.**



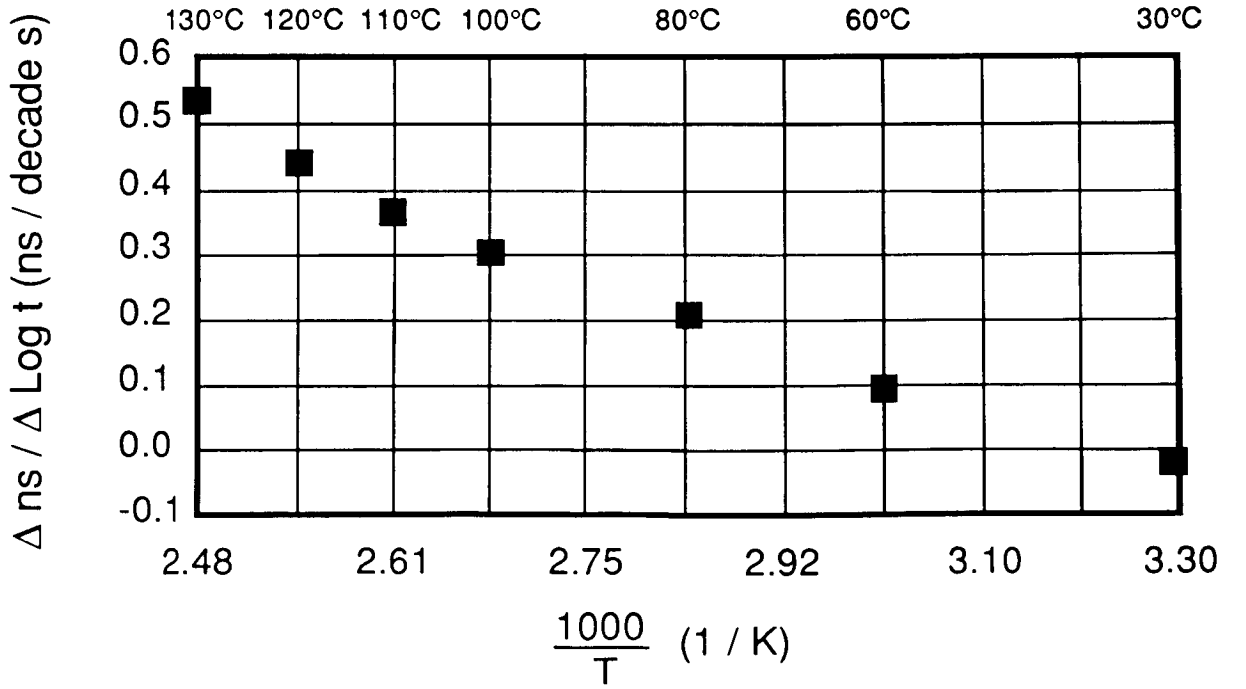
5. **Estimated time required for crystallization to proceed 50% as a function of temperature.**



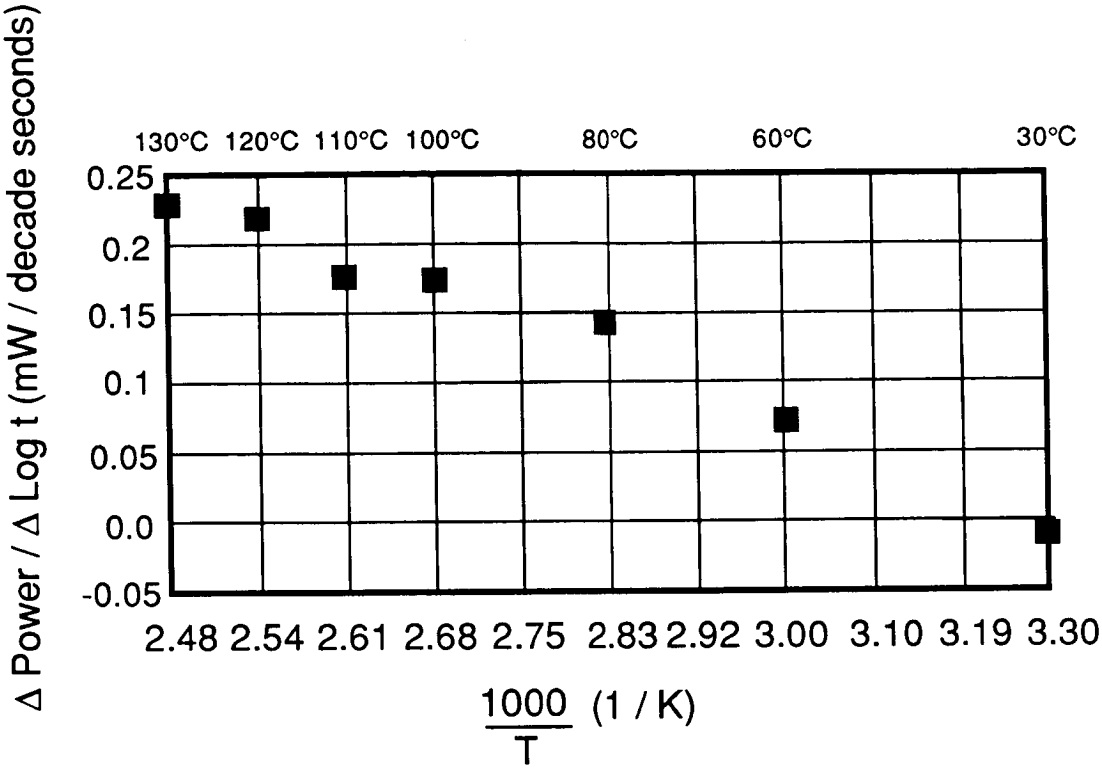
6. **TEM micrograph of (a) a laser-recorded mark in its unheated state, and (b) a mark that has been heated to 140°C for an extended period of time and that experienced extended growth of the crystalline phase beyond the original mark boundary.**



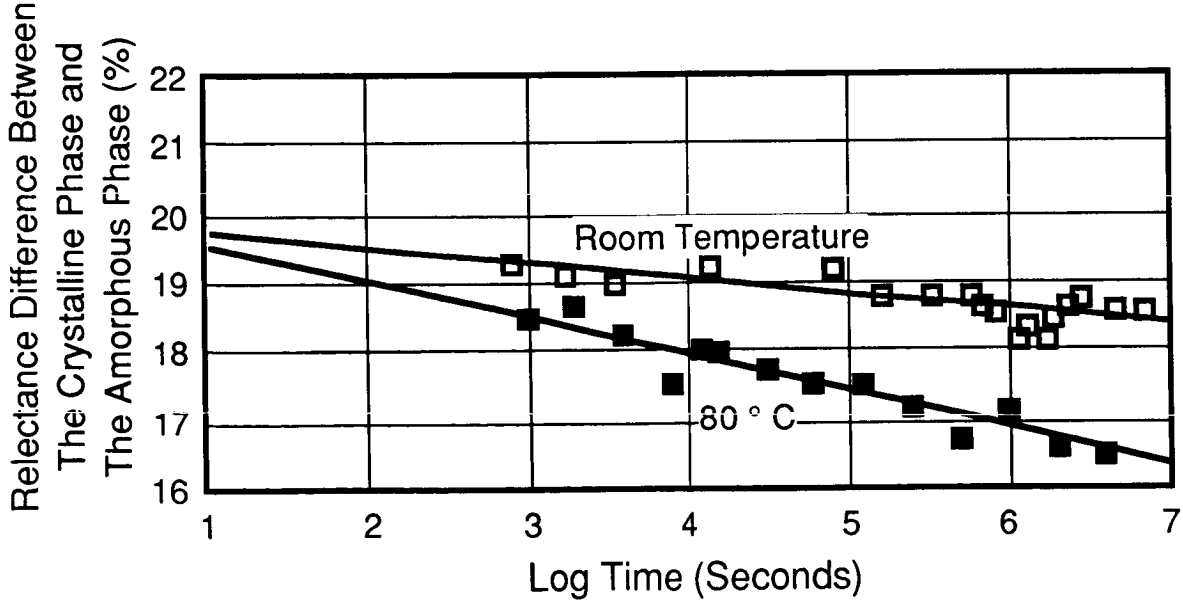
7. **Time needed for extended mark growth as a function of temperature. All points for 3 mm growth are actual data except the one at 120°C, which is extrapolated from the amount of growth observed so far. The line for 10 nm growth is estimated from the 3 mm data based on constant growth rate with time. The break in slope at 160°C is believed to be real from the many repeated experiments.**



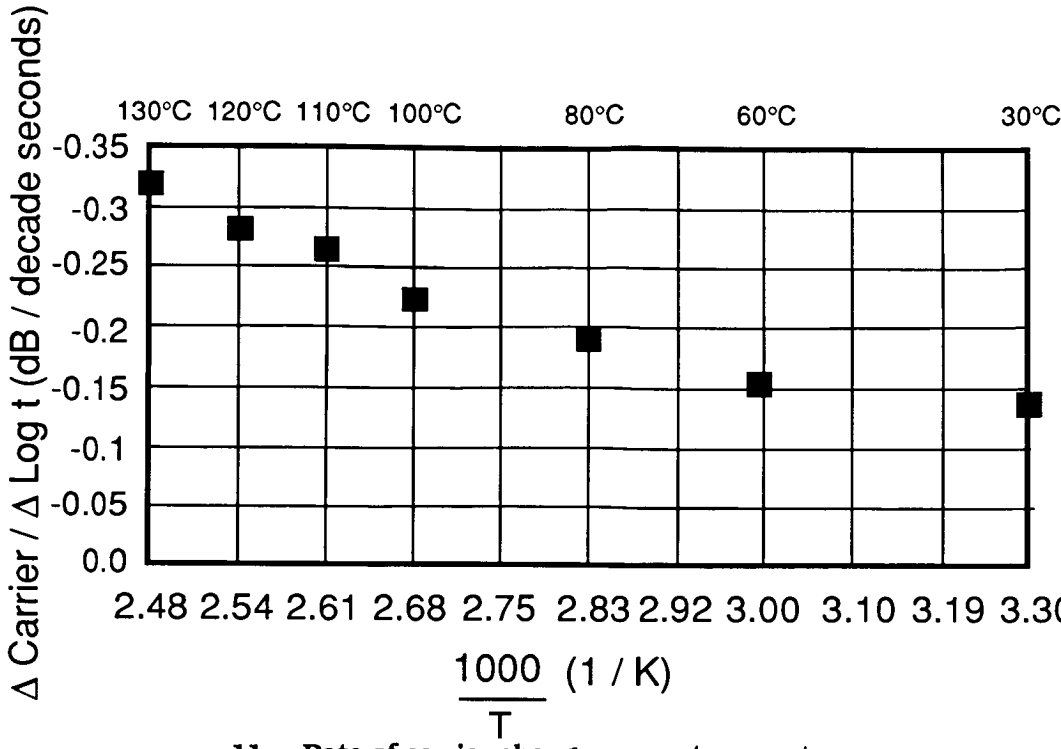
8. **Predicted growth rate due to subthreshold heating during the writing process. The rate is expressed in ns/decade, which can be converted to nm/decade of mark diameter growth by multiplying the values by the linear speed of the media, 13 m/s. The growth depends logarithmically on time which means equal amount of growth is expected between any 10^n to 10^{n+1} s.**



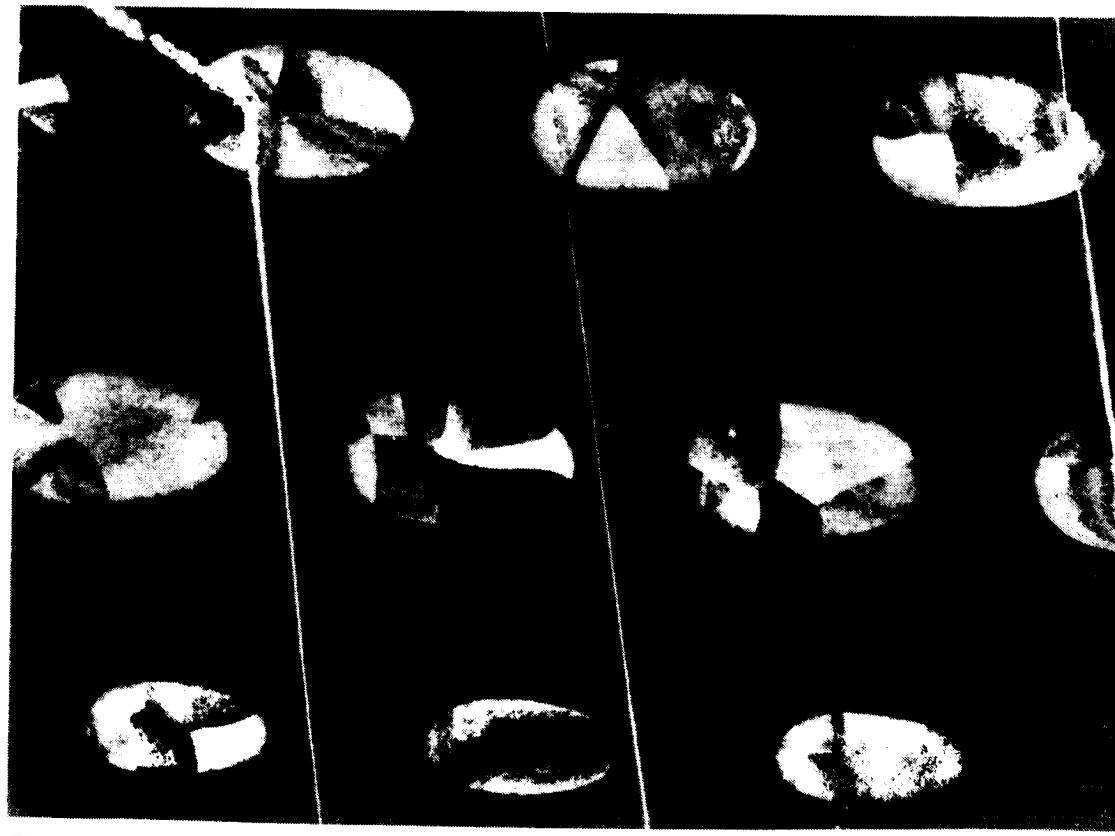
9. Change of optimum recording power as a function of time at various temperatures. The optimum recording power is defined as the power to achieve 50% duty cycle readback using 50% duty cycle input signal.



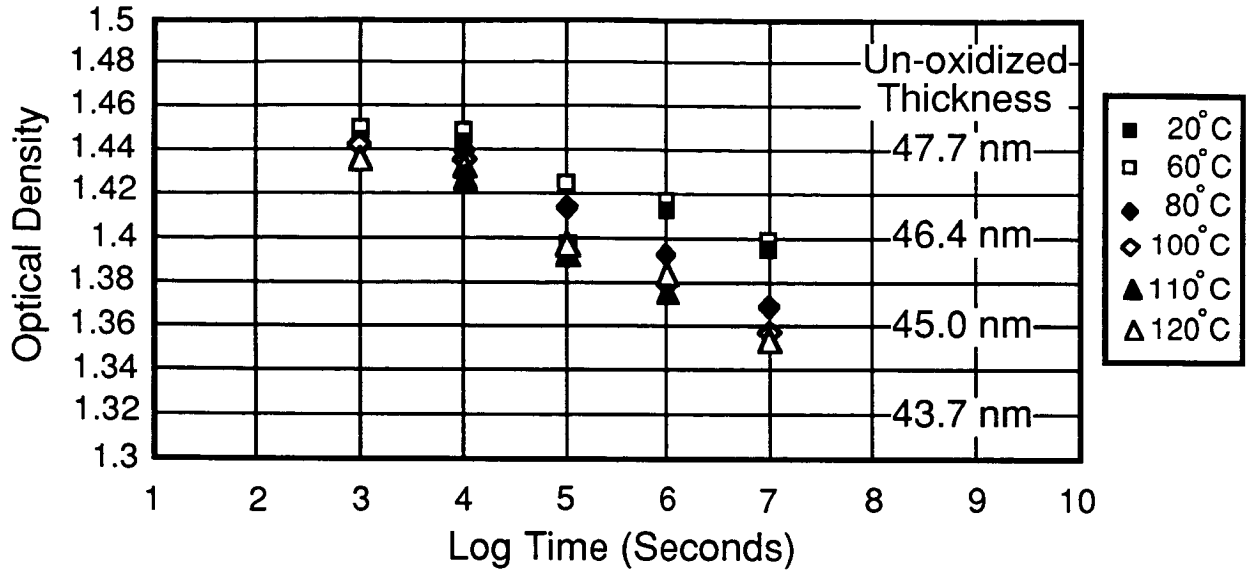
10. Change of the reflectivity of the cubic crystalline phase with time at room temperature and 80°C.



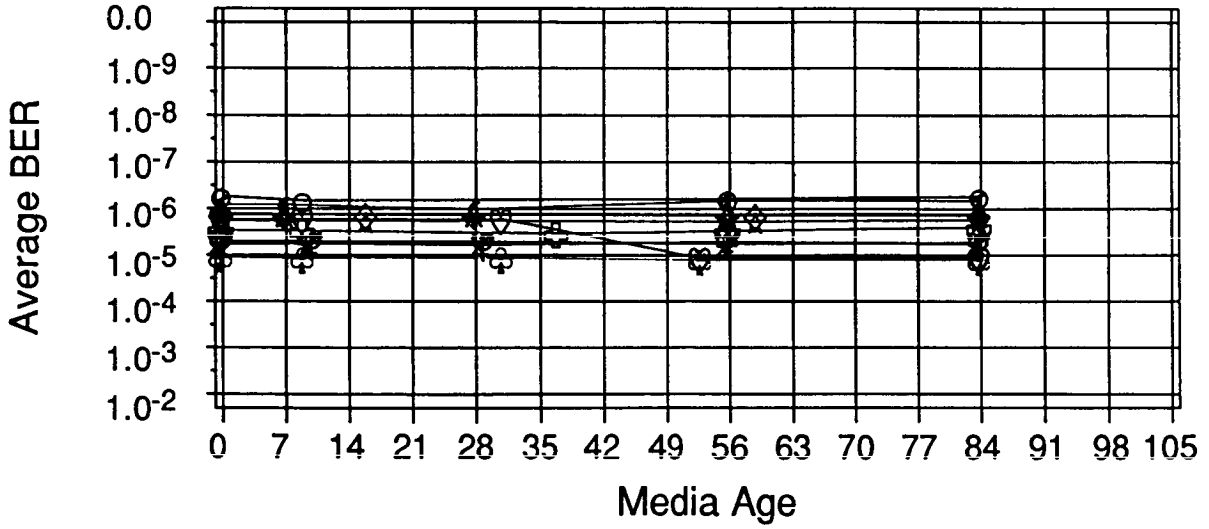
11. Rate of carrier change versus temperature.



12. TEM micrograph of laser-recorded marks after 4000 hours incubation at 70°C, 70% RH. The cracks and dark stains are results of preparing samples for the TEM studies.



13. Change of optical density for a 48-nm-thick SbInSn thin-film. The decrease in optical density is interpreted as a result of oxide formation. The remaining optical density is taken as proportional to the unoxidized film thickness.



14. Change of bit-error rate (BER) as a function of incubation time at 70 °C 90% RH for several Kodak 14" disks .