**Title:** Time Resolved Calorimetry of 30 nm Te-Films During Laser Annealing

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**Contract or Grant Number(s):** J14-81-C-0418

**Report Date:** August 10, 1984

**Number of Pages:** 800 N. Quincy Street
Arlington, VA 22217

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**Keywords:**

Calorimetry, Optical Recording

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Prepared for Publication in

Chemical Physics

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Abstract

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1. Introduction

The laser annealing of 30 nm thick Te-films has been studied using a pyroelectric thin film calorimeter [1]. Pyroelectric calorimeters are particularly suitable for the study of transient heating phenomena of thin films because of their sensitivity and time resolution. If the sample can be directly deposited onto the calorimeter it can be used as an ultrafast thermometer with a response time in the order of few picoseconds: Assuming a temperature independent pyroelectric coefficient the charge generated in a pyroelectric element is proportional to the heat content of this element and independent of the temperature distribution. For a thin film deposited onto such a calorimeter the heat flow from the film into the calorimeter is, however, proportional to the average temperature at the interface. To be able to probe the generated charge electrodes have to be deposited on both sides of the calorimeter, i.e., also between the pyroelectric detector material and the heat source, the sample. Assuming the validity of classical heat conduction processes an electrode with a thickness of 30 nm introduces due to its finite thermal diffusivity a time delay of several picoseconds. The same is true also for the heat diffusion from the sample surface to the interface between sample and electrode. With an electronic bandwidth of 100 MHz for the existing experimental setup time delay and dispersion due to thermal diffusion from the sample into the calorimeter are, therefore, negligible. The observed signal is thus within the above limits a true representation of the temperature of the sample.

2. Experimental

In this study, 9 μm thick ferroelectric PVF₂-foils (Pennwalt KYNAR®) were used as the active pyroelectric element. The PVF₂ foils were coated on both sides with a 0.3 nm Ni-electrode. The coated foil was stretched over a 8 mm diameter stainless steel supporting ring and held in place by a retaining ring. These rings served as heat sinks, electrical contacts and for mechanical support. The complete assembly was housed in a standard microbalance housing for RF-shielding.
The tellurium films in this work were thermally evaporated onto the assembled calorimeters from Knudsen cells charged with pure Te (99.9995%) source material. During the deposition the substrate was at room temperature, and the pressure in the vacuum chamber was in the order of $1 \times 10^{-7}$ Torr. The Te film thickness and deposition rate (30 nm/min) was controlled by a quartz microbalance. Films deposited under similar conditions have been found to be polycrystalline with a grain size of 100-250 nm [2]. Upon exposure to air a 2 nm thick surface layer of these films was found to be oxidized according to ESCA data [2].

Samples were excited at ambient conditions with a XeCl Excimer laser (Lambdaphysik EMG 201) at a wavelength of 308 nm. At the sample position fluences between 100 μJ/cm$^2$ and 70 mJ/cm$^2$ were achieved by suitably attenuating the raw beam. The half width of the laser pulses was determined to be 12 ns. A custom designed preamplifier (Comlinear CLC-B-600) with a 450 ps risetime and a 100 MHz transient digitizer (Dataprecision D6000) were used to record and analyze the time dependent signals.

Depending on the laser fluence typical signal shapes as shown in Fig. 1 are observed. The temperature rises almost instantaneously and depending on the initial temperature either falls continuously (Fig. 1a) or shows a plateau (Figs. 1b,c). If the plateau temperature is tentatively assigned to the recrystallization temperature of Te at 449°C the peak temperature in Fig. 1c would correspond to the boiling point of Te at 989°C.

![Figure 1: Temperature during annealing of 30 nm thick Te-films with a XeCl Excimer laser for 3 different laser fluences: (a) 0.7 mJ/cm$^2$, (b) 7 mJ/cm$^2$ and (c) 70 mJ/cm$^2$.](image)

This assignment of temperatures is supported by experiments at higher time resolution. With increasing laser fluence (Figs. 2a-2e) the sample temperature does not increase proportionally. Despite a substantial increase in laser power from 2d to 2e the same final temperature is reached. These observations are consistent with the latent heat of the assigned first order phase transitions. Tellurium being a semiconductor has of
course two different relaxation mechanisms, a fast vibrational relaxation with a ps life time and a subsequent electronic relaxation with a life time of the order of tens of nanoseconds. Figure 2d then would be consistent with instantaneous melting during the laser pulse by vibrational relaxation and subsequent heating of the molten Te to the boiling point by electronic deexcitation. To a lesser degree these two relaxation mechanisms are visible also at other fluences. To test this interpretation of the data an experiment at a wave length of 3.7 μm is under preparation which should show the effect of electronic relaxation only.

Independent of the incident laser power all molten samples cool to the same crystallization temperature (Fig. 3). The latent heat for crystallization depends of course on the amount of material lost due to evaporation. As shown in Fig. 4 the transition from crystallization to cooling by heat conduction in solidified material occurs earlier for increasing laser fluences. The largest increase in material loss is observed for Fig. 4e, the exposure with the longest boiling boiling time (Fig. 3e). In the molten phase several time constants are observed. Before the onset of crystallization one time constant which is attributed to heat conduction in liquid tellurium is observed for all samples. The initial plateau and the subsequent rapid cooling at the highest laser fluences might be due to heating of part of the calorimeter above its Curie temperature and subsequent evaporation of the sample.

Computer simulations of the heating and cooling processes using a finite differences method for the solution of the heat diffusion equation are under way. Preliminary results are in agreement with the general pulse shape observed and the peak temperatures reached. These calculations also indicate that a thin layer of the PVF₂ material should be for a short time above its melting point and, therefore, no longer pyroelectric. Measurements of the capacitance of the calorimeters before and after laser annealing did, however, not show any change in polarization. Repolarization of the depolarized thin
Fig. 3: Temperature during the liquid phase observed when annealing 30 nm thick Te-films with a XeCl Excimer laser with different laser fluences (b)-(e) as in Fig. 2.

Fig. 4: Temperature during the transition from recrystallization to conduction in the solid state observed when annealing 30 nm thick Te-films with different laser fluences (b)-(e) as in Fig. 2.
surface layer upon cooling below the Curie temperature is conceivable as a consequence of the high electric fields generated by the hot, but still polarized bulk of the calorimeter.

3. Conclusion

In conclusion, the feasibility of calorimetric studies of thin films during laser annealing has been demonstrated. The data indicate the importance of the various relaxation processes for heating of the semiconductor film and different heat transport processes during the cooling phase. In addition boiling was identified as the prevalent mechanism for the loss of material in this experiment.

4. Acknowledgments

The authors would like to thank R. Grygier and L. Kelley for technical assistance. This work was supported in part by the Office of Naval Research.

5. References

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