*__Breaking news__*

# TEMPORAL OSCILLATIONS OF THE ELECTRICAL RESISTANCE IN AMORPHOUS $SnSe_2$ THIN FILMS

M. Popescu, A. Lőrinczi, F. Sava, A. Tomescu C. Simion, G. Socol[1], E. Axente[1]
National Institute R&D of Materials Physics, 077125 Bucharest-Magurele, Romania
[1]National Institute for Laser, Plasma and Radiation Physics, MG. 54, 77125 Bucharest, Romania

## 1. Materials and methods

Recently, amorphous thin films of composition $SnSe_2$ have been prepared by pulsed laser deposition on alumina substrates. The rectangular $\alpha - Al_2O_3$ substrates ($20 \times 2$ mm$^2$) were provided with platinum electrodes on one surface. On the back side of the alumina plate a special platinum circuit with a Joule resistance allowed to heat the plate at a maximum around 500 $^oC$. The amorphous film was deposited by laser pulses. The deposition was made in a stainless steel vacuum chamber evacuated down to a residual pressure of $2 \times 10^{-6}$ Pa before each deposition. Pulses generated by a KrF* excimer laser were used in the experiments ($\lambda$ = 248 nm, $\tau_{FWHM}$ ~20 ns, f = 1Hz). The laser fluence value per pulse was 3.6 J/cm$^2$. The number of pulses was 30,000.

## 2. Conductivity measurements

The conductivity of the $SnSe_2$ films was measured in a special chamber in standard synthetic air (atmosphere composition, without water). Measurements were made at room temperature and at various temperatures up to 200 $^oC$. A Keithley electrometer and a special apparatus of type for conduction monitoring in various gases, were used to this purpose.
Four films were measured. The electrical resistance was measured in each case. The values of the resistance were collected automatically in constant conditions at every minute. The data were processed by a PC computer.

## 3. Results

Figure 1 shows the evolution during 4.5 hours of the resistance of one of the samples.
One observes a power-law decrease of the electrical resistance, from 6440 $\Omega$ down to 6200 $\Omega$ (~ 4% decrease). The sample was then heated at 50, 75, 100, 125, 150 and finally at 200 $^oC$.
At each temperature the electrical resistance at the moment of the first measurement was recorded, as well as the time evolution of the resistance during ~ 4 hours). The evolution of the electrical resistance for the case of the sample heated at 200 $^oC$ is shown in fig. 2.

## 4. Temporal oscillations of electrical resistance

Careful analysis of the resistance data recorded at room temperature points out to a surprising set of time oscillations. After extracting the continuous decreasing component of resistance, the temporal oscillations were evidenced and characterized. The temporal oscillations ($\Delta R$~f(t)) are represented in figure 3. The oscillations are very regular and their amplitude does not increase signigficantly in time. They are characterized by a period of 18 minutes and an amplitude of 4 $\Delta$. After our knowledge this is the first time when such oscillations are observed. It is remarkable that if the measurement is stopped and the sample measured after some time (typically 24 h) the time evolution of the resistance and the accompanying oscillations are reproduced.

We have analysed, also, the curve of resistance versus time for the same sample heated at 200 °C. As evident from figure 4, when compared to figure 3, no oscillations can be revealed in the last case, but only standard noise.

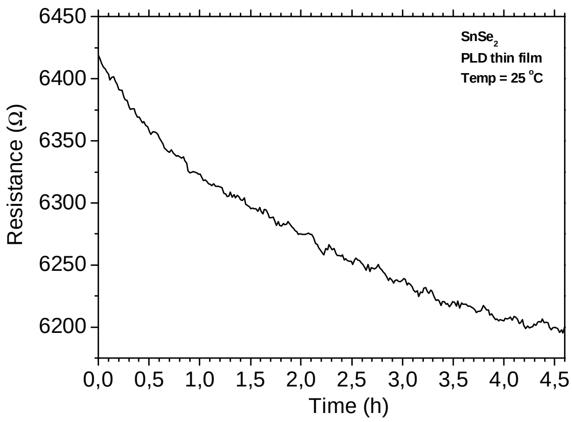



*Figure 1. The time evolution of the resistance of an amorphous thin film of composition Sn $Se_2$.*

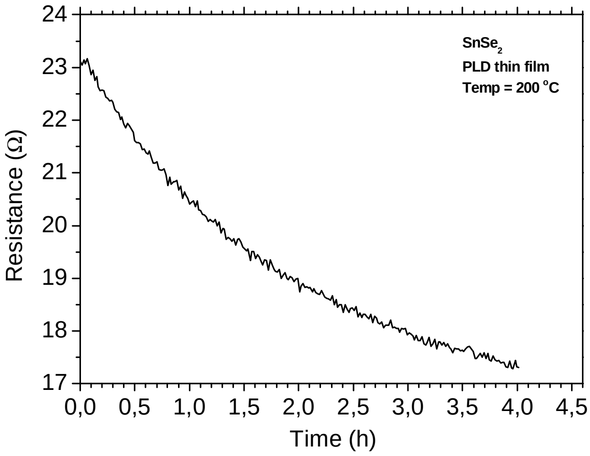



*Figure 2. The evolution of the electrical resistance of the same amorphous film heated and measured at 200 °C.*

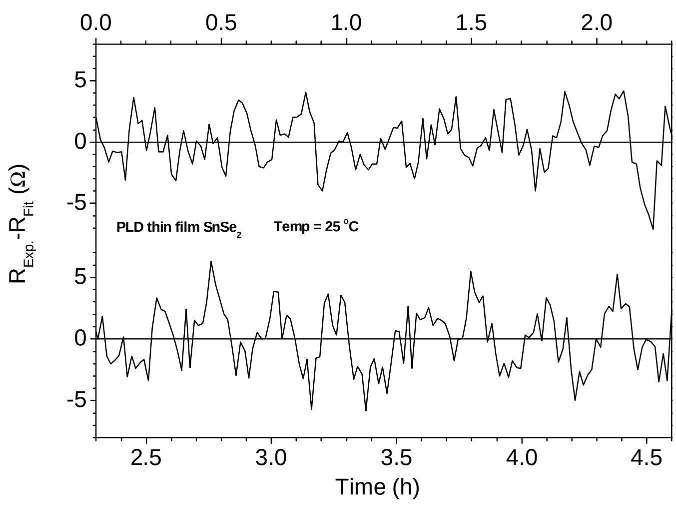



*Figure 3. The differential electrical resistance in amorphous $SnSe_2$ film. $R_{Fit}$ is the value corresponding to the point of the curve that fits the assembly of the measured points.*

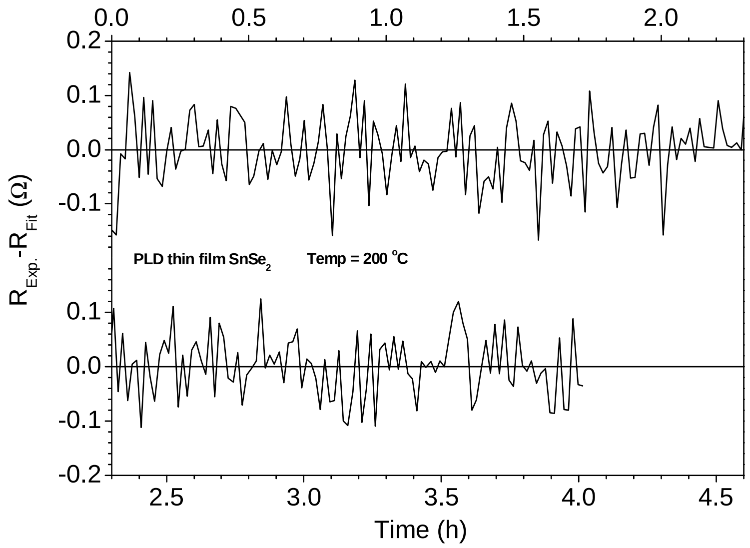



*Figure 4. The differential electrical resistance in heat treated crystallized $SnSe_2$ film and measured at 200 $^oC$. $R_{Fit}$ is the value of the point corresponding to the curve that fits the assembly of measured points.*

**5. Discussion**

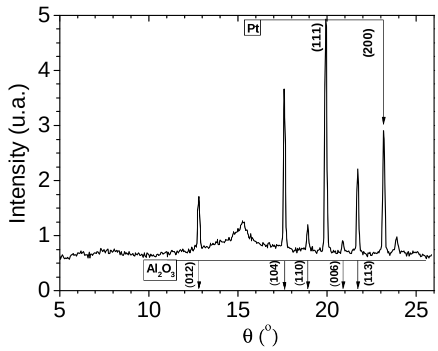
The new phenomenon observed in amorphous $SnSe_2$ seems to be related only to the disordered state of the sample. During heating of the sample, above 75 $^oC$, the amorphous structure is subjected to a transformation toward a more ordered, crystalline state. In order to prove this transformation we have measured by X-ray diffraction the structure of the film in the initial as-deposited state and in the final state at room temperature, after measurement at 200 $^oC$.

The X-ray diffraction diagram of the fresh film deposited directly on the alumina + platinum heater is shown in Fig. 5. The X-ray pattern evidences the full amorphous structure of the film. The alumina and platinum diffraction lines of the substrate, are, also, visible on the diagram. The sample heat treated, and then measured at room temperature, shows visible change of the X-ray pattern (Fig. 6): raising and narrowing of a peak at theta = 15.25 $^o$ (d= 2.929 Å), appearance of a significant peak at theta = 7.27 $^o$ (d=6.088 Å), and a peak at 23.90 $^o$ (d=1.902Å ). The three crystalline peaks were identified as peaks characteristic to $SnSe_2$ hexagonal crystal. Therefore, by heating the amorphous $SnSe_2$ film at 200 $^oC$ a transition toward $SnSe_2$ crystalline modification takes place.

The different structures of the films speak in favour of the differences in electrical behaviour of the samples. The experiences have been repeated on other samples. One of the samples has been measured also to 200 $^oC$, and other two samples were measured at room temperature, and not heated.

The observed phenomenon seems to be reproducible, but the oscillation amplitude significantly differs from sample to sample.

A possible explanation of the instability in amorphous $SnSe_2$ films is the metastable structure of the disordered network of atoms. Due to lone pair electrons of selenium, and steric freedom, the electric field can switch gradually the local atomic configurations in other configurations more stable in the electrical field and the resistance increases; as a consequence, the electrical field at the level of amorphous domains is changed; then the configurations are gradually forced back to the initial one. Such changes are not possible in the crystalline phase.



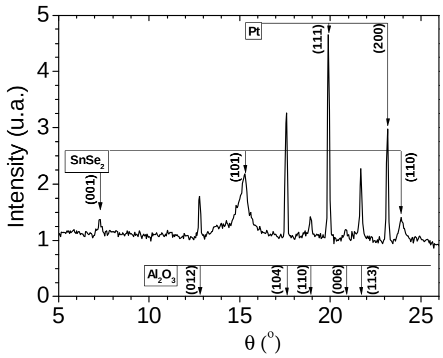




*Figure 5. X ray diffraction pattern measured at room temperature of the initial sample (not heat-treated). The measurement was performed on the twin sample depozited by PLD in the same proces.*

*Figure 6. X ray diffraction pattern of the sample treated at 200 °C and measured at room temperature.*

Finally we have compared the relaxation curves of the resistance for the same sample at room temperature and at 200 $^{o}$C. For this purpose we have normalized the two curves from fig. 1 and 2 by calculating the ratio $(R-R_f)/(R_o-R_f)$ where $R_o$ is the initial resistance, $R_f$ is the final resistance and R is the electrical resistance at every point (measured values). Thus, for all the cases, the relative resistance (RR) varies between 1 and 0. Figure 7 shows the results.

The time relaxation of resistance is not identical for the room temperature curve and for the curve recorded at 200 $^{o}$C. The most evident difference is in the middle part of the time interval. The special feature is related to more stretched exponential evolution of the curve for amorphous film (measured at room temperature). It is known from the literature that the amorphous materials exhibit stretched exponential evolution as opposite to the crystalline case. This peculiarity is related again to the disordered structure of an amorphous material, which can suffer structural arrangements, more or less hierarchically, under the action of external factors. For high temperature a phonon-assisted mechanism of conduction must be taken into account.

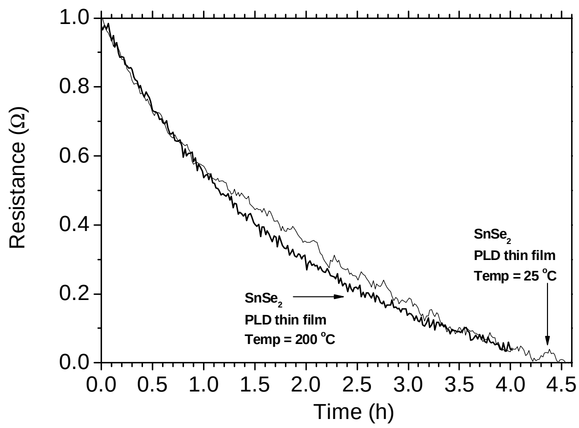



*Figure 7. Comparison between the relaxation curve of an amorphous thin film of $SnSe_2$ (see fig. 1) and that of the film heated and measured at 200 $^{o}$C (see fig. 2)*

## 6. Conclusions

Temporal oscillations of the electrical resistance have been observed in amorphous films of $SnO_2$. No such oscillations have been observed in the same films heat-treated and measured at 200 $^{o}$C. The heat-treated films exhibit a $SnSe_2$ crystalline phase.

The time evolution of the electrical resistance is characterized by a stretched exponential law for the amorphous film and simple exponential (or power-law) for the heat treated (crystallized film).