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APPLICATION OF THIN-FILM DTA TO AMORPHOUS SELENIUM LAYERS

J. PRZYŁUSKI, J. PŁOCHARSKI and W. BUJWAN

Institute of General Chemistry and Inorganic Technology, Warsaw Technical University, ul. Noakowskiego 3, 00-664 Warszawa, Poland

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A system of evaporated thin-film Ag–Bi thermocouples was used as a differential temperature sensor for DTA measurements. The crystallization of thin amorphous selenium layers was observed by means of this method. The presented method may be useful in studying the thermal transformations of thin films that have different compositions and various applications.

Solid-state samples are frequently studied by means of DTA and DSC. These methods gain specific importance in the examination of the thermal transformations of amorphous chalcogenide semiconductors [1, 2]. Standard DTA or DSC equipment is designed almost exclusively for bulk samples and, obviously, this kind of samples is usually studied. Since the practical applications of amorphous semiconductors are closely related to the thin films of these materials, there is a practical need for DTA methods designed specifically for such films.

Some work in this field has been done employing standard DTA or DSC equipment and the method of either stripping the film mechanically from the substrate surface [3] or evaporating the studied material onto thin elastic foils [4, 5]. In our opinion, the interpretation of the results of such experiments is very difficult. A promising application of thin-film Au–Ni thermocouples on a sapphire substrate has been reported by Audiere *et al.* [6].

This paper reports on studies on a system of vacuum-evaporated thermocouples, facilitating the elimination of some fundamental difficulties in thin-film DTA.

Experimental

Measuring plates were prepared by the consecutive evaporation of Ag and Bi under 10^{-3} Pa pressure onto borosilicate glass substrates. Silver and bismuth layers of 0.5 μm thickness each were shaped in the evaporation through specially designed contact masks. The pattern of conductive paths is presented in Fig. 1. A system of eight differentially connected Ag–Bi thermocouple junctions was applied.

All metallic layers except for the small silver contact areas were covered by a 1 μm thick evaporated SiO film in order to insulate them. Measuring plates were thermally stabilized by two-hour annealing at 520 K. This method of preparation of a system of thin-film thermocouples yielded a satisfactorily reproducible thermo-

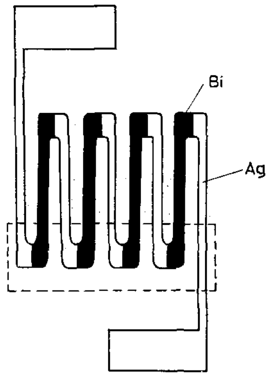

Fig. 1. Thermocouple pattern; hatched contour: tested film deposition area

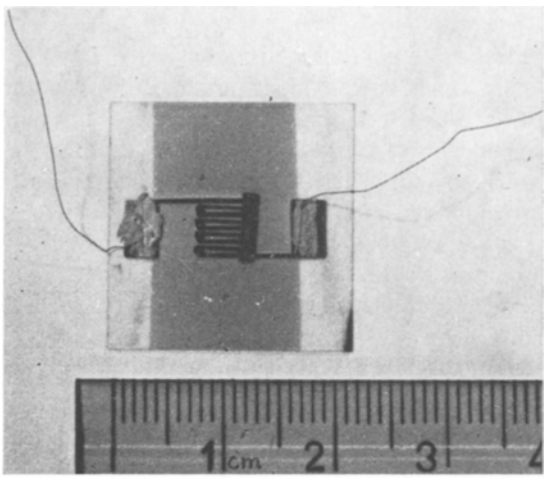

Fig. 2. Measuring plate with deposited Se film

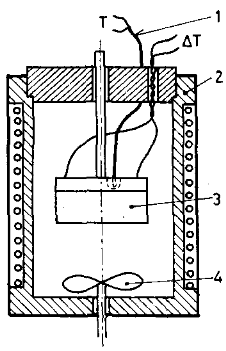

Fig. 3. DTA furnace; 1. control thermocouple; 2. furnace aluminium trunk; 3. aluminium block sample holder; 4. Stirrer

power of 0.068 mV/K per junction. The resistance of the thermocouple system did not exceed 1 kΩ.

A layer of amorphous selenium was evaporated onto one set of thermocouple junctions. A measuring plate with a deposited selenium layer is presented in Fig. 2. The plate with sufficient electrical connections was inserted into an aluminium block inside a resistance heated furnace. A scheme of this furnace is presented in Fig. 3. The temperature inside the furnace could be changed at a constant rate. A differential signal from the contact areas was registered with a sensitivity of 100 μV/m.

Results

A typical DTA curve for amorphous 1.9 μm thick selenium film obtained at a heating rate of 0.03 degree/s is shown in Fig. 4 (curve I). The glass transition shows a threshold in the DTA trace at T_g = 318 K. The recrystallization results in an exothermic peak that begins at T_x = 378 K. X-ray diffraction studies and

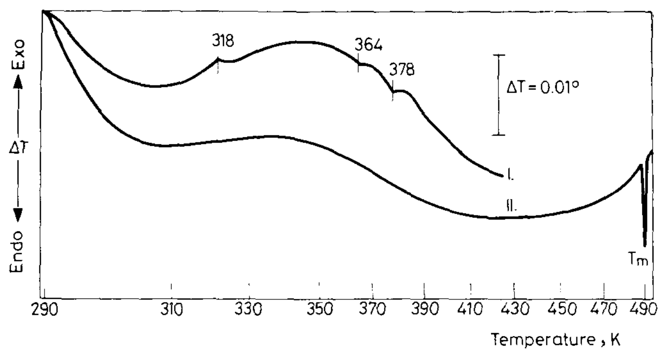

Fig. 4. Amorphous Se film DTA trace; curves I and II: first and second heating cycles, respectively; heating rate 0.03 degree/sec

microscopic observations confirm the assumption that crystallization of the amorphous phase takes place over the temperature range 380–400 K.

Curve II in Fig. 4 resulted from a second heating cycle on the same sample. The complete absence of any peaks prior to the melting point (T_m = 490 K) is consistent with the presented interpretation of curve I.

There are some suggestions [7] that the crystallization of amorphous selenium has a two-step character. Bearing this in mind, the peak which begins at 364 K seems to be related to the first step of this process; however, this is only a weak assumption.

Conclusions

The presented method has several advantages that make it especially useful for extensive application in thermal studies of thin-films. The method has some features that may be useful when examining the thermal properties of thin-films:

i) the preparation of measuring plates is simple and relatively cheap;

ii) thin-film samples can be tested without stripping them from a substrate;

iii) the amount of material required is about 20 μg, which can easily be collected in a technological process of thin-film deposition.

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Résumé — Des thermocouples en films minces évaporés Ag—Bi ont été utilisés pour la détection de la différence de température en ATD. On a observé, par cette méthode, la cristallisation des couches minces de sélénium amorphe. La méthode présentée peut être utile dans l'étude des transformations thermiques des pellicules minces de compositions différentes et d'applications diverses.

Zusammenfassung — Das System von aufgedampften Ag—Bi Dünnschicht-Thermoelementen wurde als Differentialtemperatursensor zu DTA-Messungen eingesetzt. Die Kristallisation dünner amorpher Selenschichten wurde durch diese Methode verfolgt. Die beschriebene Methode kann bei der Untersuchung thermischer Umwandlungen der dünnen Schichten verschiedener Zusammensetzungen Anwendung finden.

Резюме — В качестве дифференциального температурного сензора в измерениях ДТА была использована система тонкопленочных Ag—Bi термопар, полученных из газовой фазы. С помощью этого метода наблюдалась кристаллизация тонких аморфных слоев селена. Представленный метод может быть использован для изучения термических превращений в тонких пленках различных составов и назначений.