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Photocalorimetric measurement of the heat flow during optically and thermally induced solid state reaction between Ag and $As_{33}S_{67}$ thin films

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Abstract

Thin films of amorphous chalcogenide with composition of $As_{33}S_{67}$ (thickness $d = 300$ nm) and silver film (thickness $d = 30$ nm) on top of chalcogenide film were deposited by vacuum thermal evaporation. Prepared bilayer $Ag/As_{33}S_{67}$ was illuminated and photo-induced dissolution and diffusion (OIDD) process of silver in chalcogenide film studied by means of photocalorimetry. The heat flow connected with OIDD process during light exposure as a function of light energy, light intensity and temperature has been studied by means of photocalorimetry. The enthalpies of OIDD process were obtained and attributed to the bond energies of the formed bonds.

Keywords: Amorphous chalcogenides; Solid state chemical reaction; Photocalorimetry; Thin films

1. Introduction

Optically and thermally induced dissolution and diffusion (OIDD) of metals such as Ag (Cu, Zn) into amorphous As–S, As–Se, Ge–Se and Ge–S chalcogenide films has been extensively studied by many workers because of fundamental research and potential applications [1,2].

The OIDD process is a solid state chemical reaction in which heat seems to be measurable according to our previous results [3]. The solid state reaction enthalpy of the silver optically induced dissolution and diffusion into thin films of amorphous films of composition $As_{33}S_{67}$ has been the focus of this study. The photocalorimetric measurements have been previously used to study heat released during the photocuring of polymers [4].

2. Experimental techniques

Thin films of amorphous chalcogenide ($As_{33}S_{67}$ with thickness of 300 nm) and metal (Ag with thickness of 30 nm) on top were deposited by vacuum thermal evaporation.

The heat connected with OIDD process during light exposure by high pressure Hg lamp has been studied by means of photocalorimetry.

The photocalorimeter (PCA) was used with the TA Instruments DSC Q100 differential scanning calorimeter. This accessory allowed samples to be placed inside the DSC cell and to be irradiated with ultraviolet and visible light. The sample weights were ∼1 mg. When the bilayer sample ($Ag/As_{33}S_{67}$) was exposed to light, photo-induced solid state reaction occurred and heat was released. This heat was measured to understand the OIDD process and its kinetics [5]. The OIDD process was also independently followed by means of compositional analysis (EDX), optical transmission and Raman spectra. Energy dispersive X-ray analyzer is placed on SEM. Jeol JSM-550LV, analyzer IXRF Systems, detector Gresham

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Sirius 10. The accuracy of composition is ±0.5 at.%, as we used special low voltage procedure to avoid e-beam influence. The optical transmission spectra of the films were recorded with Jasco V-570 UV–vis–NIR spectrophotometer. Raman spectroscopy has been carried on the $As_{33}S_{67}$ films before and after silver was photo-doped into them. The Raman spectroscopy study was performed on a Fourier transformation (FT) Raman spectrometer (Bruker, model IFS/FRA 106). Raman spectra were excited using a laser beam with λ = 1064 nm having an output power 50 mW. All techniques proved the fact that solid state chemical reaction took place during light exposure in PCA unit.

2.1. PCA accessory

The TA Instruments PCA accessory is based on a filter photometer (Novacure® 2100), which contains a high pressure mercury lamp that delivers light over the spectral range 250–650 nm with different spectral range filters (300–450; >450; >520; >560 nm) and IR cut-off filter. Light is transmitted from the instrument to the DSC cell via a 0.5 m long, 3 mm diameter, dual quartz light guide. The light guide attaches to the cell itself using a special adapter.

2.2. Experimental consideration

There are several fundamental instrument characteristics that affect the quality of PCA results. Those characteristics are: wavelength range, light intensity at the DSC cell sample and reference positions, baseline noise, exposure time, and temperature.

2.2.1. Wavelength range

The Novacure® is a photometer instrument with various filters. A broadband filter supplied with the instrument covers 320–450 nm and is suitable for most UV and visible PCA studies. Visible long-pass filters with cut-offs at 450, 520 and 560 nm were also used and mounted at the DSC end of the light guide. Their optical transmissions and mercury lamp spectrum are shown in Fig. 1.

2.2.2. Light intensity

The PCA is based on a high intensity, high pressure mercury lamp capable of producing a total light intensity of about 20,000 mW/cm^2. This intensity is far in excess of that required for most photocalorimetry experiments. (Most experiments are performed with intensities between 20 and 500 mW/cm^2 at the sample.) Therefore the intensity reaching the DSC cell is adjusted using a combination of aperture control at the PCA unit and neutral density and/or cut-off filters at the end of the light guide. The light intensities at the end of each "arm" of the dual light guide must not only be regulated to the proper level, they must also be balanced to produce minimum baseline offset. The TA Instruments Q SeriesTM DSC's are based on a design that allows the heat flows at the sample and reference platforms in the DSC cell

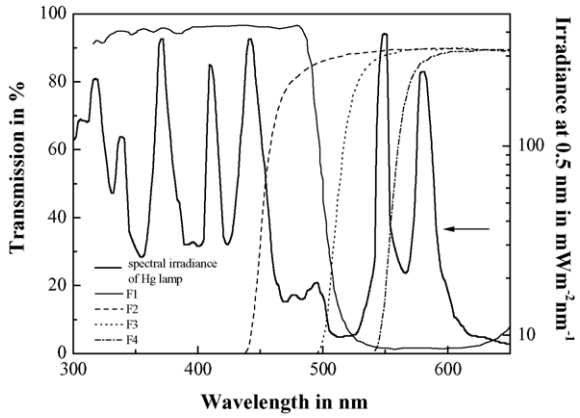

Fig. 1. Mercury lamp spectrum and visible long-pass filters transmission used in PCA experiments.

to be independently measured. In the absence of a sample or reference material and pans (i.e., an empty cell), the heat flows observed are directly related to the light intensities at the platforms. Therefore the actual intensity experienced by the sample can be determined. In addition, the intensities at the sample and reference platforms can be balanced by a simple adjustment on the cell light guide adapter.

2.2.3. Baseline noise

Ideally, the light intensity delivered to the DSC cell through the light guide should be constant. However, the high pressure mercury lamp used in the PCA has some inherent fluctuations in its output. The DSC cell is sensitive enough to detect those small fluctuations in light intensity as noise in the heat flow baseline. There is no system adjustment that can be made to eliminate this noise. Fortunately, the noise is typically less than +100 μW/cm^2, which has no effect on the heat flows associated with the photoinitiated events being studied since these heat flows are several orders of magnitude larger.

2.2.4. Exposure time

Photoinitiated curing reactions are fast thermal events. Complete cure is achieved in several seconds to several minutes. This can make differentiating the curing behavior of similar materials difficult even if low light intensities are used. The ability to vary exposure time, therefore, provides an additional experimental variable that can help improve the differentiation of different types of behavior, and/or provide conditions that are closer to those found in real-world processes (e.g., photocuring of a film coating as the film rapidly passes under a light source). The PCA connects to the DSC cell via an event cable that opens and closes a shutter at the light source. Exposure times as short as 0.6 s can be selected in the PCA method.

2.2.5. Temperature

Most PCA experiments were run isothermally. The PCA is compatible with the FACS and RCS coolers. PCA exper-

iments can be performed in the temperature range −50 to 120 °C. Furthermore, once the PCA experiment is complete, a standard DSC experiment can be run on the fully/partially cured sample material over the broader temperature range covered by the selected cooler by making only a few minor changes to the system.

2.2.6. Dual sample operation

The unique design of the DSC Q Series TM instruments allows the heat flows at the sample and reference platforms to be independently measured. This provides the ability to measure and balance the light intensities at the cell platforms. In addition, this ability to independently measure heat flows allows the PCA to be used for dual sample operation. Dual sample operation is primarily used when comparing similar materials under a specific set of experimental conditions (wavelength range, light intensity, temperature, and exposure time) to evaluate the effects of different types or concentrations of photoinitiators. Results are captured in a single data file as two different heat flow signals [heat flow A and heat flow B].

3. Results

We started the PCA accessory experiments with a test of sensitivity of the OIDD process with illumination of samples at different light intensities with filter F1 (Fig. 1), as shown in Fig. 2. We observed the saturation of the heat flow under higher intensities at 280 and 450 mW/cm^2. We have also run tests to find best spectral range where the OIDD process is most efficient, as shown in Fig. 3. The optical transmission of the bilayer Ag/$As_{33}S_{67}$ samples has been also measured, as shown in Fig. 4. It is known that most efficient energy of light that induces the OIDD process is in the absorption edge of the amorphous chalcogenide film. The comparison of the spectral cut-off edge of the filters and the absorption edge of the bilayer sample shows that filter F2 should be used for all

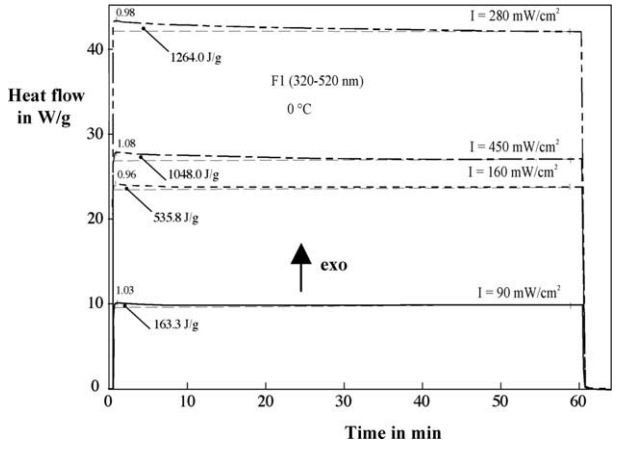

Fig. 2. Typical PCA heat flow curves during OIDD process for different mercury lamp intensities at 0 °C using filter F1 (spectral range 320–450 nm).

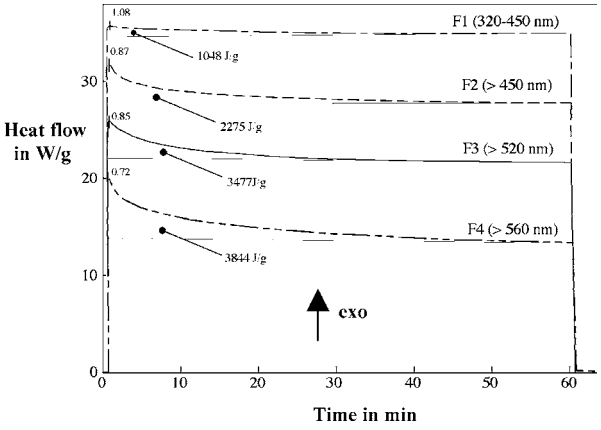

Fig. 3. Typical PCA heat flow curves during OIDD process for a constant mercury lamp intensity (450 mW/cm^2) at 0 °C using different filters.

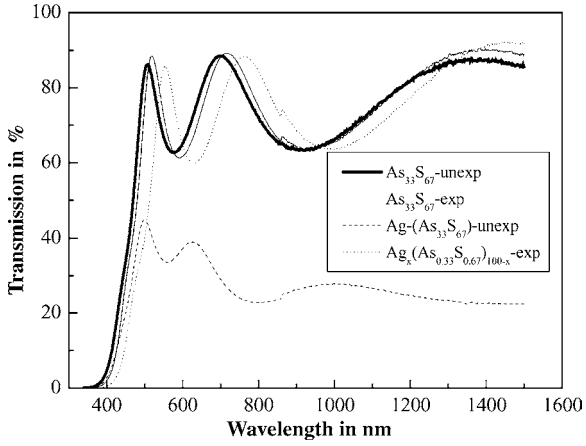

Fig. 4. Typical optical transmission curves of the films before and after PCA experiments.

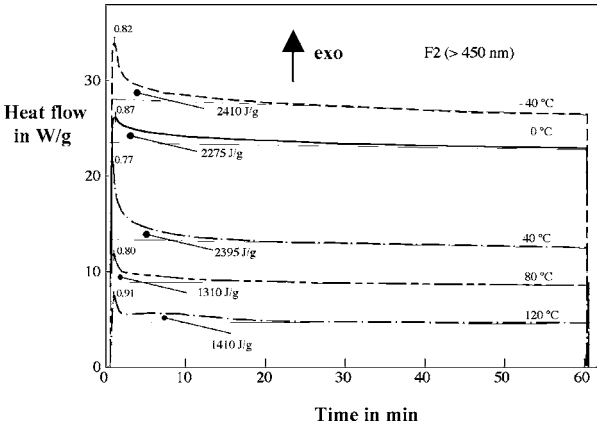

Fig. 5. Typical PCA heat flow curves during OIDD process for constant mercury lamp intensity (450 mW/cm^2) using filter F2 (>450 nm) run isothermally at different temperatures.

other experiments (see Fig. 1). The PCA accessory allowed us also to study OIDD process isothermally at different temperatures, as apparent from Fig. 5. The characteristic shape of enthalphic flow versus time behavior was an abrupt increase

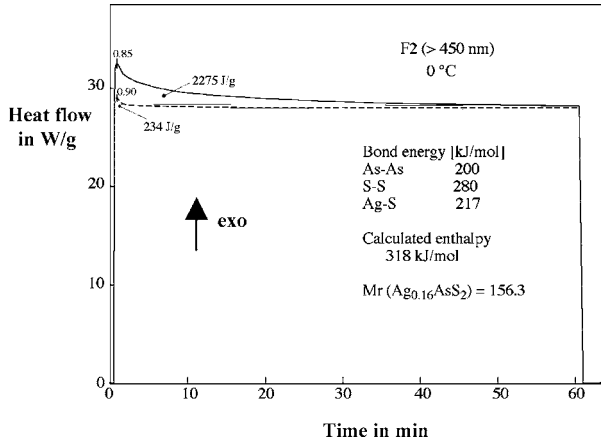

Fig. 6. Typical PCA heat flow curves during OIDD process for constant mercury lamp intensity (450 mW/cm^2) using filter F2 (>450 nm) run isothermally at 0 °C and repeated scan on the already illuminated film.

to a maximum value followed by a slow temporal decay. The total amount of the heat was obtained by the integration of the area bellow the isothermal exothermic heat flow curve. All heat flow curves were similar in the temperature range between −40 and 80 °C. The heat flow curve at 120 °C, as shown in Fig. 5 exhibits two characteristic maxima.

The PCA measurements were also run twice with the same sample at two different temperatures, 0 and 120 °C as shown in Figs. 6 and 7, respectively. The amount of enthalpy in the first photocalorimetric scan of the sample is one order of magnitude higher than that in the second "repeated" scan at both temperatures. Furthermore, once the PCA experiment was completed, a standard DSC experiment was run on the fully reacted sample material over the temperature range from 50 to 300 °C as shown in Fig. 8. DSC experiment shows a clear glass transition temperature T_g and two cold crystallization regions T_{c1} and T_{c2} typical for the Ag–As–S system.

The PCA accessory allowed a dual sample operation (see Section 2.2.6). The bilayer Ag/$As_{33}S_{67}$ samples and a sample that consisted of a single $As_{33}S_{67}$ film were placed into the

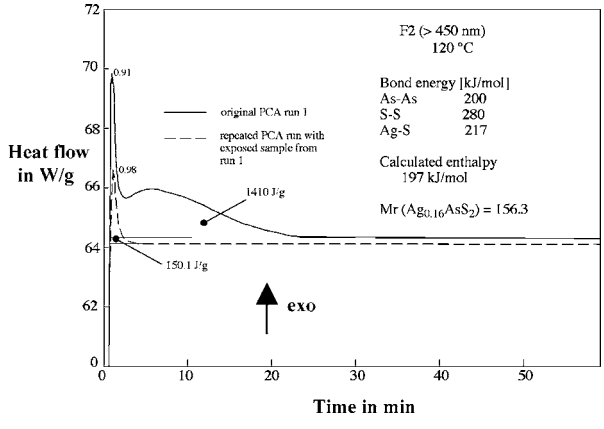

Fig. 7. Typical PCA heat flow curves during OIDD process for constant mercury lamp intensity (450 mW/cm^2) using filter F2 (>450 nm) run isothermally at 120 °C and repeated scan on the already illuminated film.

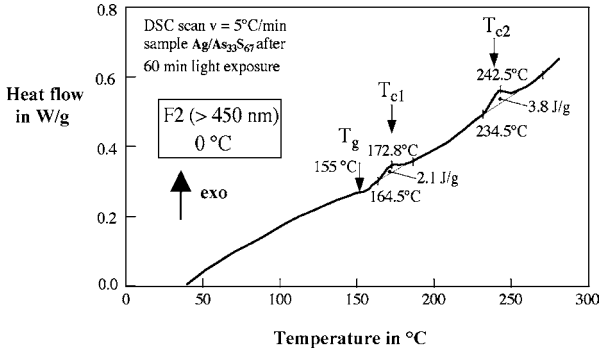

Fig. 8. Typical DSC scan on the fully reacted sample film over the temperature range between 50 and 300 °C.

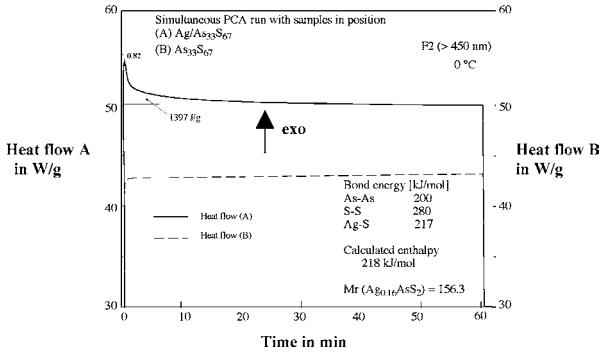

Fig. 9. Typical PCA heat flow curves as a result of dual sample operation (see Section 2.2.6) for the sample with bilayer Ag/$As_{33}S_{67}$ and sample with single layer $As_{33}S_{67}$ were placed into sample and reference pan. PCA curves were recorded during OIDD process for constant mercury lamp intensity (450 mW/cm^2) using filter F2 (>450 nm) and run isothermally at 0 °C.

sample and reference pans of the PCA cell, respectively. The results are captured in a single time scan as two different heat flow signals heat flow A and heat flow B) as shown in Fig. 9. There is a clear difference between the two heat flow curves in Fig. 9. While the silver-containing film shows a typical

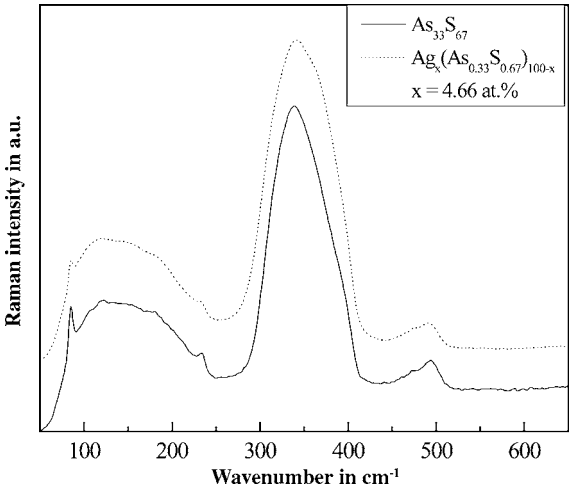

Fig. 10. Raman spectra were recorded on $As_{33}S_{67}$ and Ag-$As_{33}S_{67}$ samples after illumination in PCA units.

enthalpic peak while it is illuminated in the PCA unit, the single $As_{33}S_{67}$ film does not show any heat flow change.

Both optical transmission, shown in Fig. 4 and Raman spectra, shown in Fig. 10 were taken on samples before and after illumination in the PCA unit. Photoinduced solid state reaction between Ag and $As_{33}S_{67}$ film is reflected in the red shift of the absorption edge in Fig. 4 and in a decrease of intensity of characteristic bands at 475 and 490 cm^{-1} in Fig. 10, which are assigned to sulphur rings and sulphur chains.

4. Discussion

The PCA experiments, in our opinion, have clearly shown the ability to measure the heat released as a result of the photoinduced solid state reaction as a part in the optically induced dissolution and diffusion (OIDD) of silver in amorphous $As_{33}S_{67}$ films. The OIDD is a complex process [6], which includes Ag^+ ion formation, as illustrated in Fig. 11, as a part of the chemical reaction $2\,Ag + S \rightarrow Ag_2S$, in which $\Delta G^\circ_{298} = -19.09$ kJ/mol. The formation of Ag–S bonds is also part of the solid state chemical reaction $Ag + AsS_2 \rightarrow AgAsS_2$, when the stoichiometric compound or a solid solution with a composition of stoichiometric compound is formed. Measured PCA enthalpies (J/g) in Figs. 6, 7 and 9 were recalculated in terms of molar amounts of the final film compositions as shown in Table 1. The final enthalpies are typical for the OIDD processes and are shown inside Figs. 6, 7 and 9. The calculated values of enthalpies are approximately between

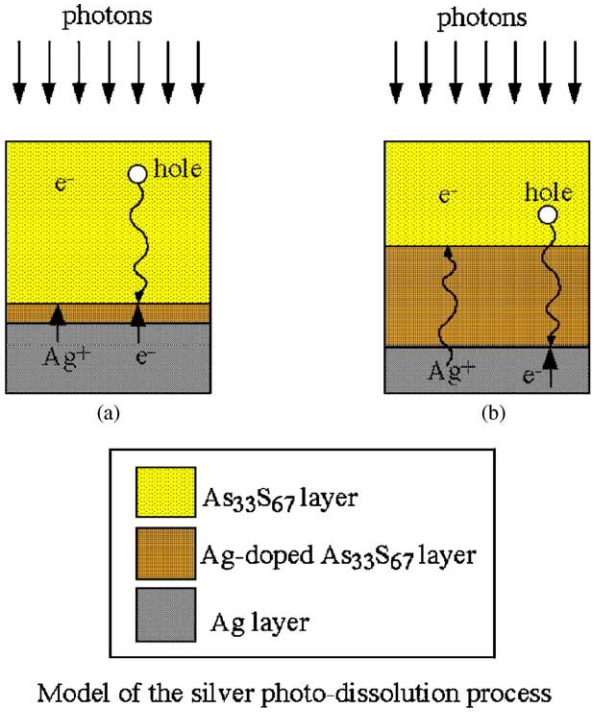

Fig. 11. Schematic illustration of Ag^+ ions formation during OIDD process.

Table 1
Composition of the films before and after PCA experiments was established by EDX analysis

Film	Ag (at.%)	As (at.%)	S (at.%)
$As_{33}S_{67}$	–	32.371	67.629
$Ag_x(As_{0.33}S_{0.67})_{1-x}$	4.659	31.31	64.031

200 and 300 kJ/mol and are in reasonable agreement with the Ag–S, As–As, S–S and As–S bonds energies [7]. Such bonds are broken or formed during OIDD process as it was shown by the Raman spectra (Fig. 10) and in a previous paper [8].

5. Conclusion

It has been shown that the TA instruments photocalorimer with Novacur light source can be used to readily monitor the rate of change of enthalpy of an optically induced solid state chemical reaction between films of silver and amorphous $As_{33}S_{67}$ films. The time evolution of the heat flow of the solid state reaction was measured different illumination spectra, and as function of light intensity and temperature. We were able to calculate the enthalpy value related to the bond energies broken or formed during OIDD process.

PCA cell has been used to illuminate the films for optical and Raman spectroscopy and conventional DSC measurement. The PCA results in conjunction with film composition analysis and also with Raman spectra, indicate clearly that there is an optically induced solid state reaction between Ag and $As_{33}S_{67}$ films.

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