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Thermal investigations of active compounds in thin-layer photovoltaic modules (CdTe and $CuInSe_2$)

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Abstract

Copper indium diselenide ($CuInSe_2$) and cadmium telluride (CdTe) are semiconductor compounds used in the manufacture of thin-layer photovoltaic modules. The objective of this study was to characterise the thermal behaviour of $CuInSe_2$ and CdTe which are used in photovoltaic modules, by simulating accidental fires during operation or (municipal) waste incineration. The substances were investigated by means of simultaneous thermal analysis in air and argon atmosphere.

Keywords: TA; TG; CdTe; $CuInSe_2$; Semiconductor

1. Introduction

Solar cells are considered to be non-polluting since they are able to directly convert sunlight to electric energy. Nevertheless, the production of silicon-based solar cells is quite time- and energy-consuming and accompanied by hazardous emissions.

A new technology, based on thin films of compound semiconductors. e.g. copper indium diselenide ($CuInSe_2$) or cadmium telluride (CdTe), seems to overcome this problem [1]. These materials may also bear ecological risks [2]. In cases of accidents or wrong handling, namely incineration and fires, hazardous substances may develop and be emitted to the environment [3]. For this reason, we studied the thermal behaviour of two active semiconductors, used in this new technology.

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2. Experimental

2.1. Thermal analysis

For the studies of the thermal behaviour of the samples we used a simultaneous thermal analysis/mass spectrometry device consisting of a STA 429 simultaneous thermal analyser (Netzsch Gerätebau GmbH) and an on-line coupled QMG 420 quadrupole mass spectrometer (Balzers Hochvakuum GmbH). The samples were heated from ambient temperature up to 1000 C using a heating rate of 5 K min^{-1} in an argon atmosphere and synthetic air. For this investigation the weight of the sample was about 100 mg.

2.2. Sample materials

$CuInSe_2$ powder was a gift from Research Triangle Institute (Research Triangle Park, NC, USA) with a purity higher than 99.999%. CdTe powder with a purity higher than 99.99% was purchased from Heraeus (Darmstadt, Germany).

3. Results and discussion

3.1. Copper indium diselenide

The thermal degradation of $CuInSe_2$ in air occurs in two steps from ambient temperature to 800°C. The first weight loss in Fig. 1 at a temperature below 100°C is related to the moisture in the sample. The two degradation steps of about 8.4 and 27.1% of the total sample amount can be explained as follows.

After correction, the mass losses of 9.0% and 29.1% of the dry sample occur. Thus the first step of the degradation seems to be a partial oxidation of the sample. The oxidation

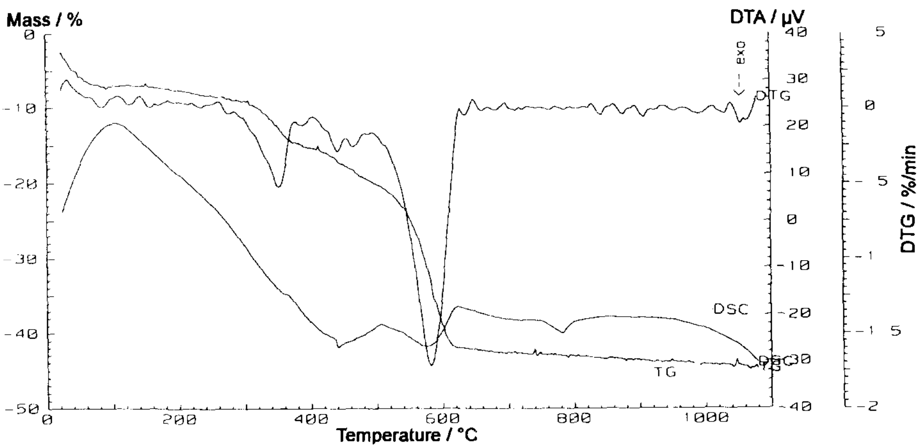

Fig. 1. TA curves of $CuInSe_2$ in synthetic air.

given in Eq. (1) leads to a theoretical mass loss of 9.4%. In the second step a total oxidation (theoretical mass loss 28.1%) of the sample can be assumed (Eq. 2).

$$2CuInSe_2 + 1.5O_2 \rightarrow 2CuInSe_{1.5}O_{0.5} + SeO_2 \uparrow \quad (1)$$

$$2CuInSe_{1.5}O_{0.5} + 4.5O_2 \rightarrow 2CuInO_2 + 3SeO_2 \uparrow \quad (2)$$

$CuInSe_2$ not being thermodynamically stable in the presence of oxygen has already been described. Oxidation at temperatures between 150°C and 300°C leads mainly to In_2O_3 and SeO_2. At the oxide/$CuInSe_2$ boundary, the formation of Cu_xSe was observed [4]. The structure $In_2O_3/Cu_2Se/CuInSe_2$ was also proved for oxide layers at room temperature except that SeO_2 could not be detected [5].

The degradation of the sample in argon atmosphere is quite different due to the absence of oxygen. At about 150°C the weight of the sample increases by about 0.3% of the total sample mass. At about 350°C it decreases in the same range being constant up to a temperature of 800°C. Then a mass loss of about 3% can be obtained up to 1000°C (cf. Fig. 2). Further heating of the sample leads to the evaporation of the material.

This evaporation of $CuInSe_2$ at lower temperatures compared to $CuInSe_2$ in the presence of oxygen may be due to a higher stability of oxidic phases to evaporation or sublimation. Our attempts to detect evaporating elements or compounds failed probably due to the kind of coupling of the DTA to the mass spectrometer. However, the formation of thermodynamically favourable compounds like InSe, $InSe_2$ and CuSe is described in the literature to be expected during production of the active layer of solar cells by vapour deposition techniques [6]. In our experiments we should expect the reverse situation.

The TA values from the investigation in air and argon atmosphere are listed in Table 1.

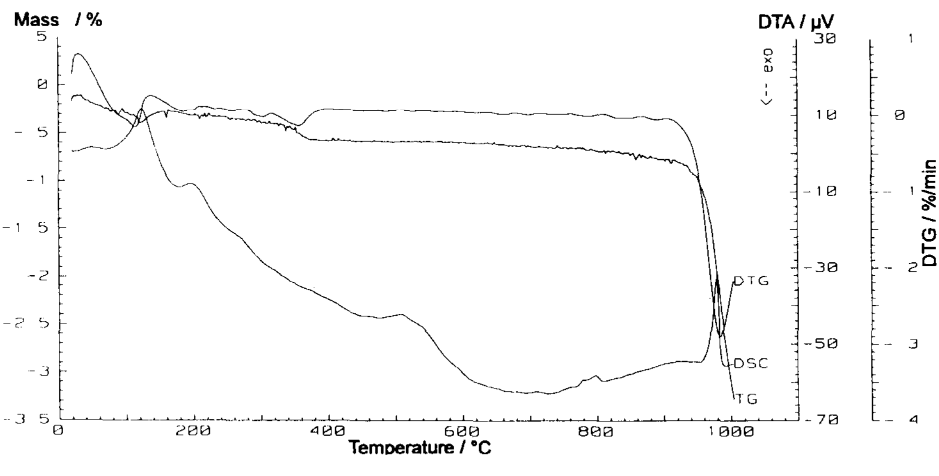

Fig. 2. TA curves of $CuInSe_2$ in an argon atmosphere.

Table 1

TA data obtained from $CuInSe_2$

T_i/°C	DTA_{max}/°C	DTG_{max}/°C	Δm/%
Synthetic air			
250	441; 574; 783	352; 583	−8.4; −27.1
Argon atmosphere			
650[b]	123[a]; 212[a]; 930[a]	356; 984	+0.3; −0.3; −2.6

[a] Endothermic.
[b] Start of 2nd weight loss.

3.2. Cadmium telluride

The thermal behaviour of CdTe differs from that of $CuInSe_2$. In air, at about 600°C an increase of weight can be obtained, which is forced at about 700°C. At about 800°C a total increase of 19% can be obtained. This oxidised product remains stable up to 1050°C and then decreases in weight. From the increase in weight, the oxidised form can be assumed to be an almost complete oxidation to $CdTeO_3$ (Δm_{th} = 20%).

The degradation in argon did not show an increase in weight (Fig. 4) in the temperature range investigated. Around 850°C a mass loss of the sample starts. The degradation occurs in two steps and leads to a total loss of the sample. From these results an evaporation of the sample can be assumed. More than 80 years ago the high volatility of Cd in CdTe was described which leads to difficulties in the determination of the melting point at 1041.5°C [7]. The effect in the DTA curve obtained at about 1150°C could not be explained up to now. It does not correspond to the melting point or to the boiling point at 1091°C [7]. The TA values are summarised in Table 2.

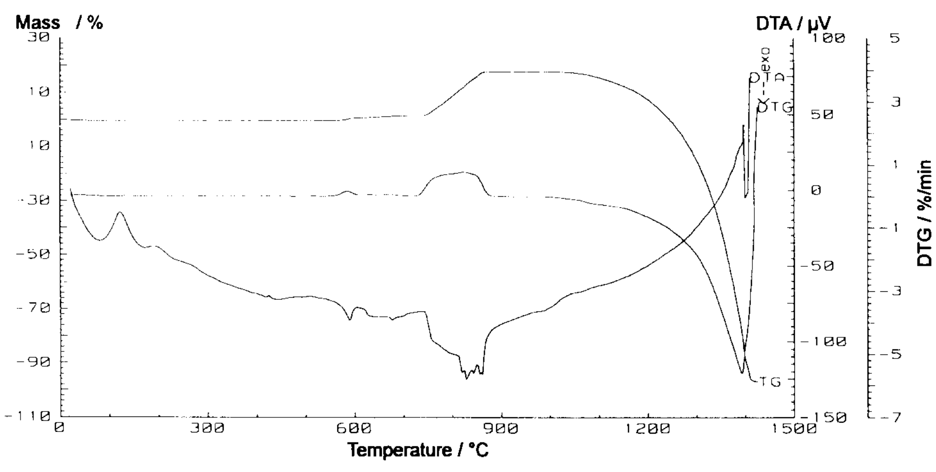

Fig. 3. TA curves of CdTe in synthetic air.

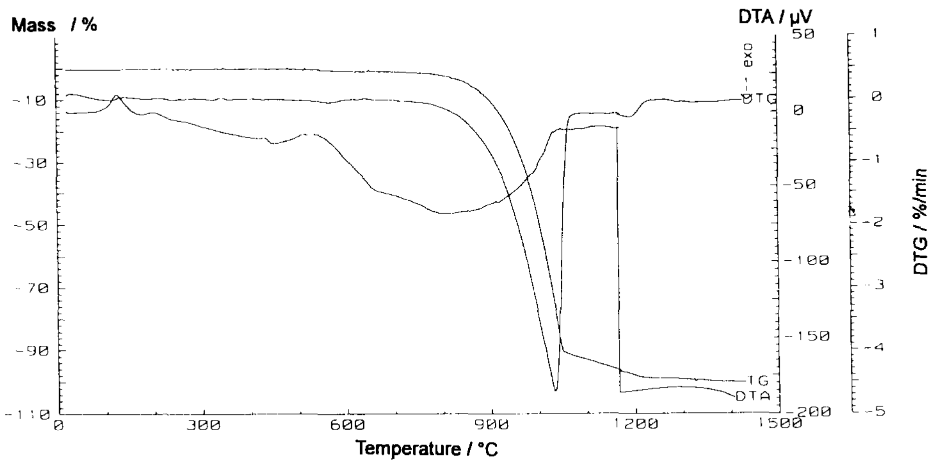

Fig. 4. TA curves of CdTe in an argon atmosphere.

For CdTe in air the starting point for the decrease in weight is higher than for CdTe in argon atmosphere. This effect can be explained by the formation of oxides which are less volatile than the pure compound or the elements, e.g. the boiling point for CdO is between 900 and 1000°C which is a consequence of the still high volatility of Cd (melting point of CdO > 1500°C) compared to 765°C for Cd [7].

4. Conclusions

The investigation of the thermal behaviour of the compound semiconductors CdTe and $CuInSe_2$ in our experiments showed a release of substances at high temperatures. Under oxidising conditions both compounds are more stable with respect to volatilisation. However, $CuInSe_2$ releases SeO_2 at rather low temperatures. Under non-oxidising conditions both compounds are evaporated at temperatures in the range where accidental fires occur, which is assumed to be up to 1000°C.

Table 2
TA data obtained from CdTe

T_i/°C	DTA_{max}/°C	DTG_{max}/°C	Δm/%
Synthetic air			
550	122[a]; 590	823; 1393	+16.8; −114.8
Argon atmosphere			
800	126[a]	1033; 1192	−91.8; −6.0

[a] Endothermic.

Further investigations will have to demonstrate which species of the elements may be emitted under more realistic conditions of thermal treatment.

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