BNL-111859-2016-CP

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Presented at the SPIE Optics & Photonics 2016 Conference
San Diego Conference Center, San Diego, CA
August 28th –September 1st, 2016

Aug. - Sept. 2016

Nonproliferation and National Security Department
Radiation Detector and Nonproliferation R&D Group

Brookhaven National Laboratory

U.S. Department of Energy
USDOE National Nuclear Security Administration (NNSA),
Office of Nonproliferation and Verification Research and Development (NA-22)

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Regularities in the melting and crystallization of CdTe-Al alloys

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ABSTRACT

Using differential thermal analysis, we investigated the parameters of the processes of melting and crystallization of the CdTe-Al system near the CdTe side (CdTe + 2 mol. % Al, CdTe + 4 mol. % Al, and CdTe + 6 mol. % Al). By varying the melts' intermediate isothermal holding temperature for 10, 30, and 60 minutes whilst heating them up to 1423 K, we determined the conditions needed for the melts' full homogenization. We demonstrated that increasing the Al content changes the mechanism of the melting of the CdTe phase.

Keywords: CdTe-Al, differential thermal analyses, isothermal holding, superheating, clusters

INTRODUCTION

AIIBVI compounds, in particular cadmium telluride, are some of the most widely used among all other semiconductor materials. The main fields to which they contribute are IR optics, room temperature X- and γ-ray detectors, optoelectronics, nonlinear optics, and photovoltaics.[1, 2]. By appropriately doping the CdTe, we can tune the optical and electrical properties of the material over a broad range. Using solid solutions based on CdTe allows us to obtain the desired values of the band-gap for different applications.

It is well known that a system of solid solutions of CdTe-In offers great potential for improved electron lifetimes and enhanced electrical resistivity compared to undoped CdTe[3]. Similar to In, such compensatory action was shown[4] for other Group-III elements, namely aluminum, which provides the material with high resistivity. Thus, using aluminum as a donor impurity to obtain material with n-type conductivity and high resistivity is a promising approach as an alternative to In, or as a co-dopant with In. However, the solid-solution system CdTe-Al still has not been investigated adequately[6]. Perhaps, this lack is caused by the complexities in synthesizing this type of material and by the active interaction of aluminum with oxygen.

The aim of our work was to synthesize CdTe-Al alloys with a relatively small Al content (<6%) and to investigate their melting and crystallization particularities by differential thermal analysis (DTA). Use of this technique allows us to determine the phase transformations during heating / cooling near the melting point of CdTe, the temperature range of the solid solutions' melting and crystallization, and the kinetics of the processes. Having such data is important in allowing us to predict the properties and methods of synthesis and production of semiconducting alloys of CdTe-Al crystals. In addition, despite numerous studies of the Cd-Te system, there still is continuing discussion on the placing of its solidus and liquidus lines, and the precise value of CdTe's melting point[7, 8].

EXPERIMENTS

We synthesized batches of CdTe-Al (m = 5 g) at 1393 K from pre-made high-purity CdTe and elemental Aluminum in graphite crucibles that were placed in quartz ampoules. The ampoules then were evacuated to 10^{-3} mbar. The material for differential thermal analyses in amounts of 500 mg next was quantitatively moved to graphitized ampoules for the DTA and then sealed, leaving a minimum of free space.

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Hard X-Ray, Gamma-Ray, and Neutron Detector Physics XVII, edited by
Larry Franks, Ralph B. James, Michael Fiederle, Arnold Burger, Proc. of SPIE Vol. 9593,
95931B · © 2015 SPIE · CCC code: 0277-786X/15/$18 · doi: 10.1117/12.2187488

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DTA measurements were conducted on an automated DTA setup similar to that described in[9]. The experiments were carried out with a heating/cooling speed of 10 K/min. A separate series of investigations were carried out using controls by a programmable Maxthermo MC2738 thermocontroller within the range of ± 0.5,K from the set temperature. We used S-type thermocouples (platinum/platinum + 10% rhodium) to measure the temperature. Each measurement was repeated three times.

RESULTS AND DISCUSSION

Figs. 1a-d show typical thermograms of the phase-melting process of pure CdTe and CdTe-Al in a dynamic heating regime. The sharp breaks in the thermograms of the CdTe samples after heating at 1366 and 1379 K demonstrated the sensitivity of the DTA apparatus to both the large endothermic effect of melting and the small additional endothermic effect that is peculiar to the melting process[10-14]. Increasing the aluminum content in the system proportionately diminishes the endothermic effect at the start of the melting process and increases the baseline curvature. This compounds the difficulties in precisely determining the "melting point" of the solid solution from the thermograms. So, the "melting points" can be estimated as 1358, 1342 and 1339 K in the case of CdTe + 2 mol. % Al, CdTe + 4 mol. % Al, and CdTe + 6 mol. % Al, correspondingly (Figs. 1b-d). It resembles the situation with indium as the dopant in CdTe[14]. However, opposite to the indium effect the aluminum doping prevents any additional endothermic contributions peculiar to CdTe melting process. Interestingly, according to the data in Figs. 1b-d, the temperature of the crystallization of the CdTe phase crystallization became "insensitive" to the increase in the content of doping impurities (1357, 1360 and 1359 K for the alloys with 2, 4 and 6 mol. % Al, correspondingly) and even exceeds the "melting temperature". Considering that that one of the reasons of such discrepancy can be the non-equilibrium of the heating process, we heated the sample up to 1423 K with an intermediate isothermal dwell to determine the precise temperature of the phase transition of these alloys. For example, an endothermic effect is registered even after a rather high temperature dwell of 60 minutes of the CdTe + 2 mol % Al melt (Fig. 1e). Therefore, we systematically investigated the kinetics of the CdTe-based phase melting and crystallization processes for these alloys (Fig. 2).

We used three isothermal holding durations (10, 30 and 60 minutes) to determine the time required for the system to shift to equilibrium after the start of the melting of the CdTe phase. Comparing the area of the "full" endothermic effect in the thermogram of dynamic heating, S_{total} (see examples in Figs. 1b-d) with the area of the endothermic effect after heating the sample after the dwell S_{dwell} (Fig. 1e, marked in green), we can determine the volume fraction (φ) of solid-like species (clusters) with strong bonds that remain in the melts. Thus, the φ value was defined as the ratio of the melting peak area S_{dwell} after an intermediate isothermal dwell to the total area of the melting peak obtained under dynamic heating conditions S_{total}. The dwell temperature dependencies of φ for three alloys we investigated after various dwell durations are shown in Fig. 2.

According to the data in Figs. 2a-c , the CdTe phase begins to melt near 1330, 1300, and 1290 (±1) K in the alloys with 2, 4, and 6 mol. % Al, which is considerably lower than "melting points" we estimated in thermograms of dynamic, non-equilibrium heating (Figs. 1b-d). Fig. 2 also presents the temperature of the system's complete transformation into a liquid (at 1370, 1365, and 1362 K, correspondingly), wherein the φ value reaches zero. As was expected, in most cases the longer duration that the system dwelled at an intermediate high temperature resulted in a lower value of φ. The higher the dwell temperature, the shorter the duration of dwell time that is needed. Therefore, Figs. 2(a-c) indicate the conditions of a sufficiently rapid transition of the system to the equilibrium state, which may be caused by the influence of aluminum atoms in the solid-phase structure.

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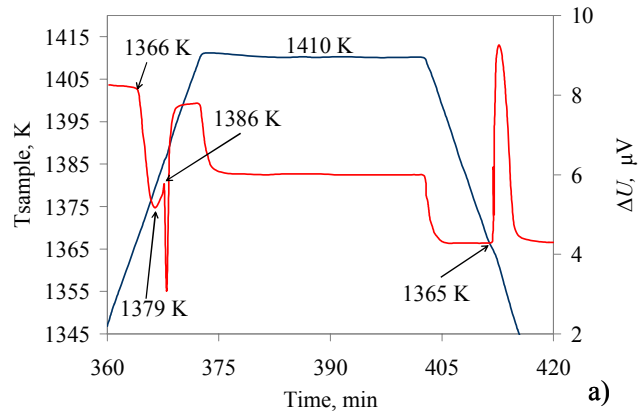

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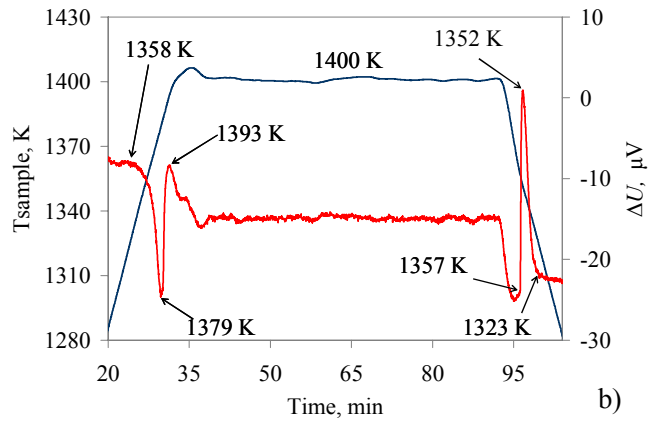

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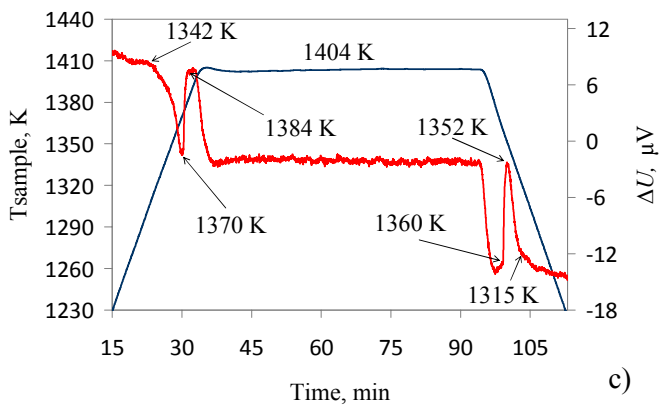

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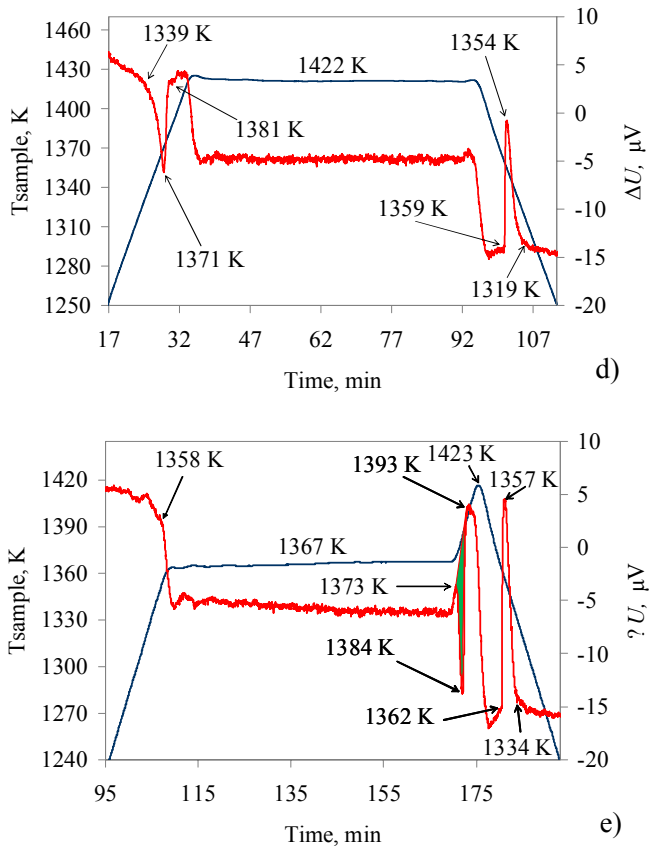
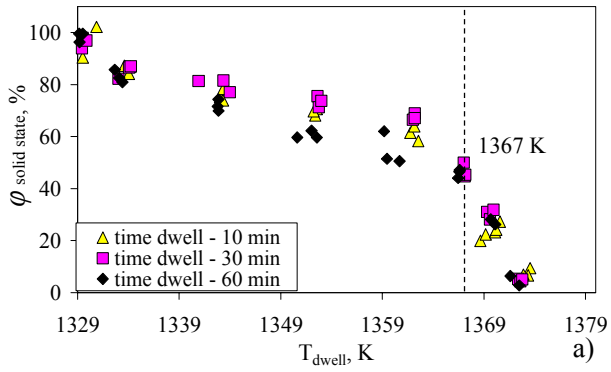


Fig. 1. Typical thermograms of the melting and crystallization of CdTe (a) and CdTe-Al alloys: b, e) - CdTe + 2 mol. % Al; c) - CdTe + 4 mol. % Al; d) - CdTe + 6 mol. % Al in dynamic heating regime and with intermediate isothermal holding (e) followed by next heating to 1423 K

Comparing the logarithmic dependencies of the volume fraction of the remaining solid phase in the melt versus the reciprocal dwell temperature (Figs. 2d-f), we see that the slope of the straight line sharply changes at a certain temperature for each of the three samples. Such temperatures are indicated in Fig. 2 by dotted lines. That situation is similar to the one for pure CdTe and CdTe with addition of 2 mol. % Ge or Sn[13]. This bend denotes a change in the mechanism of the solid phase melting with the rise in temperature. Probably this break indicates the existence of various structural units in the melts at higher and lower temperatures compared with the temperature of the break. The data of Figs. 2d-f also leads us to a conclusion about the difference in the mechanism of melting of the CdTe phase between the alloy with 2 mol. % Al and in those that contain 4 and 6 mol. % Al.



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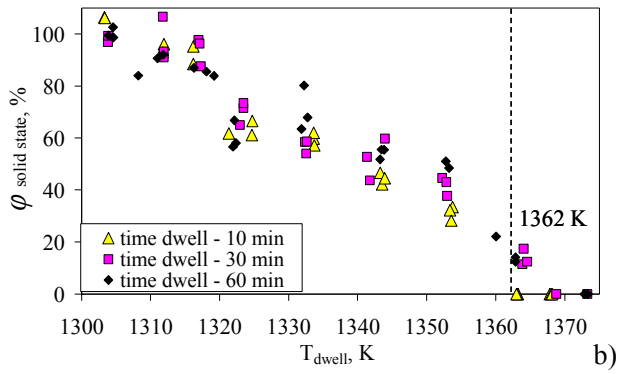

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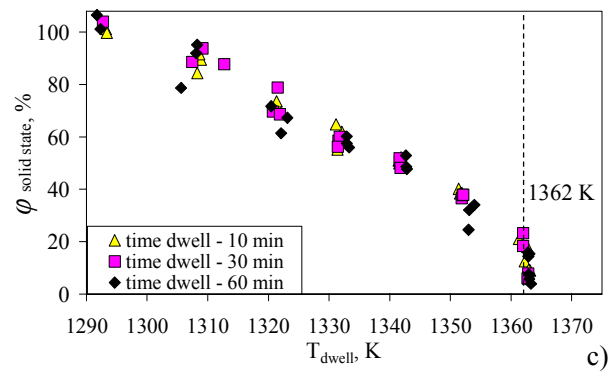

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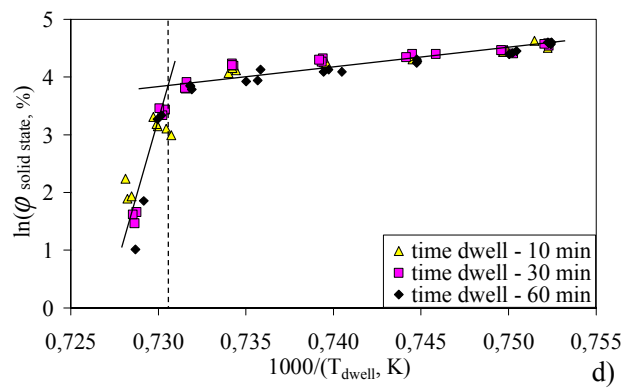

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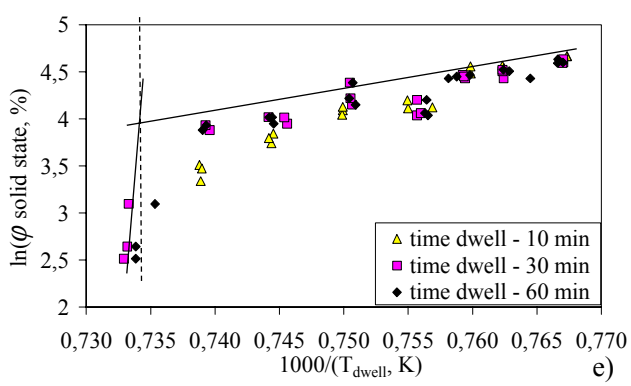

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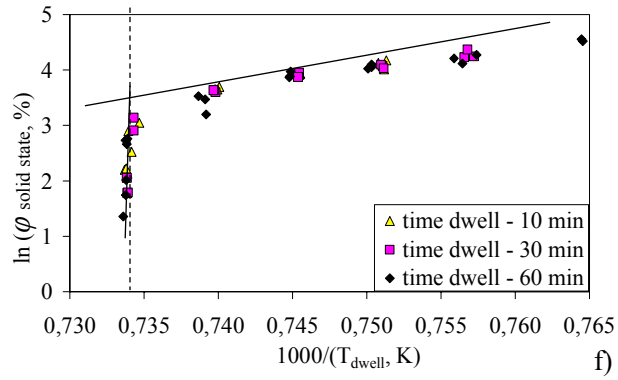
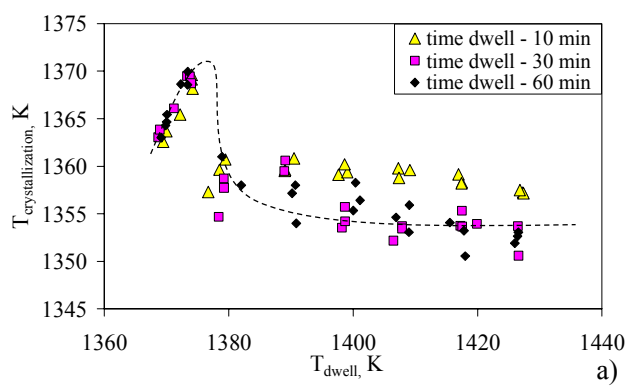


Fig. 2. The temperature dependencies of φ solid state in (a, d) CdTe + 2 mol. % Al, (b, e) CdTe + 4 mol. % Al, and (c, f) CdTe + 6 mol. % Al melts after the isothermal dwell.

This conclusion is confirmed by another DTA experiment, namely by the correlations between the temperatures of the CdTe phase crystallization T_s and the system's dwell temperature T_{dwell} (Fig. 3). As illustrated in Fig. 3, lower dwell temperatures cause crystallization at higher temperatures. In general, T_s declined when T_{dwell} increased. It signifies that the applied thermodynamic conditions are enough to assure full homogenization of the melt. However, the mutual co-location of atoms needed for rapid nucleation during next cooling is preserved in the liquid phase.

A different situation is observed in the alloy CdTe + 4 mol. % Al (Fig. 3b). At low dwell temperatures, crystallization occurred near the temperature of the dwell demonstrating the "memory" of the melt "crystal-like" structure. Only at rather high superheating (1370 – 1420 K) did this "memory" disappear and T_s stabilized independently on a superheating value. Similar regularities can be observed in the case of CdTe + 6 mol. % Al case (Fig. 3c). Thus, we can define the temperature ranges wherein the liquids became two-structural systems (amorphic matrix and crystal-like clusters), and the temperatures of the melts where they show full homogenization.

and the temperatures of the melts' full homogenization.



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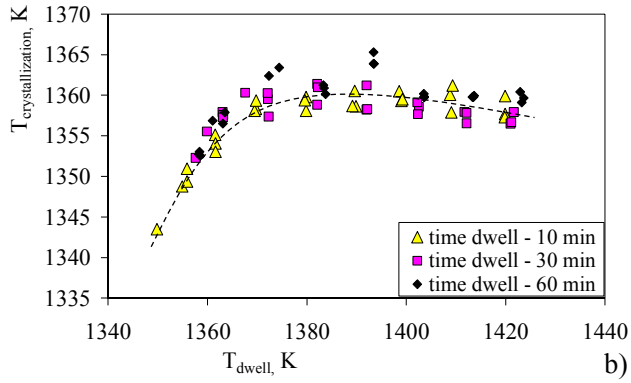

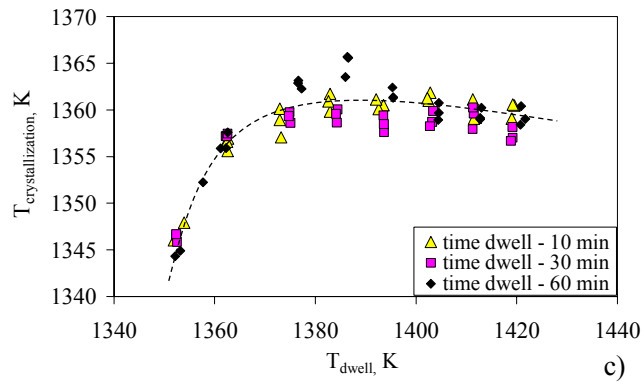

Fig.3. Temperature of crystallization versus temperature of dwell dependences for (a) CdTe + 2 mol. % Al, (b) CdTe +4 mol. % Al, and (c) CdTe + 6 mol. Al %.

Consequently, we have established the melting temperature of alloys CdTe + 2, 4, 6 mol. % Al that respectively are 1329, 1300, and 1290 K. We assume that in those alloys with higher aluminum content, a second phase with an unexplored composition exists that has a melting temperature of 1362 K. Moreover, the melts of the investigated alloys may contain some structural formations or forms of self-organized atoms of liquid that are based on aluminum. They serve as a prerequisite for the future formation of crystalline phases in the melt. The duration of the isothermal holding has no substantial influence on these processes.

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