

Reaction kinetics of α -CuInSe₂ formation from an In₂Se₃/CuSe bilayer precursor film

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Abstract

The reaction pathway and kinetics of α -CuInSe₂ formation from a glass/In₂Se₃/CuSe polycrystalline bilayer precursor film were investigated using time-resolved, in situ high-temperature X-ray diffraction. Bilayer glass/In₂Se₃/CuSe precursor films were deposited on thin glass substrates in a migration enhanced molecular beam epitaxial deposition system. These films were then temperature ramp annealed or isothermally soaked while monitoring the phase evolution. The initial In₂Se₃ and CuSe reactant phases were directly transformed to α -CuInSe₂ without any detectable intermediate phase. Kinetic parameters were estimated using the Avrami and parabolic diffusion controlled reaction models. The parabolic reaction model fitted the experimental data better than the Avrami model over the entire temperature range (230–290 °C) of the set of isothermal experiments, with an estimated activation energy of 162 (\pm 5) kJ/mol.

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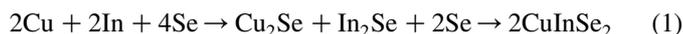
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1. Introduction

Chalcopyrite α -CuInSe₂ (CIS) and its alloys with Ga or S are proven absorber materials for high efficiency thin film solar cells. Interestingly, a variety of processing sequences have been demonstrated to form α -CuInSe₂ (e.g. co-deposition of elements, annealing of stacked elemental layers, direct compound formation, and selenization of metal particles). Furthermore, the processes are robust to small fluctuations in process conditions. This versatility is made possible, in part, by the complex Cu–In–Se phase diagram, which exhibits equilibria between α -CuInSe₂ and eight different solid phases as well as a Se-rich liquid at 773 K [1–3]. Furthermore, the α -CuInSe₂ phase field has a rather large range of solid solution, suggesting a point defect chemistry that includes significant compensation of electronic defects. An examination of equilibrium pathways for the formation of CIS, however, is unable to fully explain this versatility, and thus kinetic limitations are also important. While there have been several

studies on the mechanism for forming CIS, the detailed reaction pathways and kinetics are not yet fully understood.

To date, most studies on the mechanism of CIS formation have been performed using ex situ methods [4,5], which give limited kinetic information. Recently, various in situ techniques have been used to investigate the reaction mechanism of CIS. Based on in situ high-temperature X-ray diffraction (HTXRD) analysis, Katsui and Iwata [6] suggested the following reaction pathway for CIS formation from glass/Cu/In/Se stacked elemental layers:



Brummer et al. [7] employed in situ high-energy powder diffraction to investigate the phase transformation of three binary systems (Cu–Se, In–Se, Cu–In), ternary CIS and quaternary CIGS system using the stacked elemental film precursors (e.g. glass/Cu/In/Se, glass/Cu/Se, glass/In/Se and glass/Cu/In). They reported several intermediate phase transformations with temperature and the tetragonal CuInSe₂ formation temperature of 375–385 °C. Wolf et al. [8] used thin film calorimetry for the in situ monitoring of reaction kinetics of CIS formation from Cu/In/Se precursor. Using a Kissinger analysis, they suggested an activation energy of 160 kJ/mol with around 15% statistical error. Our research group has been

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conducting a systematic study of the reaction pathways and kinetics of the formation of CIGS and its subsystems from various types of precursors using time-resolved, in situ high temperature X-ray diffraction. In one study [9], the formation of CuInSe_2 from the bilayer structure InSe/CuSe showed that a non-crystalline intermediate phase, most likely amorphous CuInSe_2 , appeared during the initial stage of the isothermal heating in air in the temperature range 220–270 °C. Data analysis based on the Avrami and the parabolic rate law models supported a one-dimensional diffusion controlled reaction mode. The combined amorphous and crystalline CuInSe_2 interfacial layer functions as a diffusion barrier as well as a nucleation barrier. In this study, the kinetics of CuInSe_2 formation from an $\text{In}_2\text{Se}_3/\text{CuSe}$ polycrystalline bilayer precursor was studied using both temperature ramp and isothermal soaking (230–290 °C).

2. Experimental

2.1. Precursor preparation

Migration enhanced epitaxy (MEE), a variant of classical molecular beam epitaxy (MBE), was used to grow the precursor films. As in MBE, an ultra high vacuum environment and effusion cells are employed to generate molecular beam fluxes of elemental sources. In MEE, however, the substrate is sequentially exposed to each source through revolution of a platen containing the substrate, rather than a simultaneous co-deposition from all the sources. The sequence of deposition for each rotation is as follows: first the Cu source is encountered, followed by the In and Ga source, and then by the Se source. Another important distinction is that the rotating platen of the MEE system passes each substrate through a flux-free zone after exposure to the metal fluxes, and then again after the Se flux. These relaxation zones allow adsorbed atoms more time to migrate and find more energetically favored configurations. The direction of rotation can be either clockwise or counter-clockwise, so that the sequence of deposition may be reversed.

It is also noted that the MEE reactor is capable of accommodating multiple substrates (up to nine) positioned on a large rotating platen. The base pressure of the system was established at 8×10^{-9} Torr, and the pressure during deposition was in the range 10^{-7} to 10^{-8} Torr depending on the operating conditions. Further details of the deposition technique and experimental apparatus are given elsewhere [10].

Bilayer glass/ In_2Se_3 /CuSe precursor films were deposited on sodium-free thin glass substrates (Corning 7059) in the MEE reactor. Glass substrates with a thickness of 0.4 mm were employed to minimize the temperature difference and response time between the strip heater and the precursor film in the HTXRD furnace used for subsequent characterization. The samples were fabricated by first depositing a crystalline In_2Se_3 film at a substrate temperature of ~ 360 °C under ultra high vacuum conditions (10^{-7} – 10^{-8} Torr). This was followed by deposition of a crystalline CuSe film on the as-grown In_2Se_3 layer at a lower substrate temperature (~ 150 °C) to minimize the potential reaction between the In_2Se_3 and CuSe layers. The total bilayer film thickness (~ 800 nm) was measured by TEM as shown in Fig. 1, and the atomic composition of each monolayer (bottom In_2Se_3 : $[\text{Se}]/[\text{In}] \sim 1.4$; top CuSe: $[\text{Se}]/[\text{Cu}] \sim 0.93$) and bilayer ($[\text{Cu}]/[\text{In}] \sim 0.94$; $[\text{Se}]/[\text{Metal}] \sim 1.2$) film was measured by inductively coupled plasma (ICP) emission spectroscopy. The stable structure of both In_2Se_3 and CuSe at the growth temperature is hexagonal. XRD characterization of the precursor films revealed a highly textured (001) crystalline- In_2Se_3 /crystalline-CuSe bilayer structure as shown in Fig. 1.

2.2. Time-resolved, in situ high temperature X-ray diffraction

The high temperature XRD system used for the temperature ramp study consisted of a PANalytical X'Pert Pro MPD θ/θ X-ray diffractometer equipped with an Anton Paar XRK-900 furnace and an X'Celerator solid state detector. The high-temperature X-ray diffractometer used for the isothermal study consisted of a Scintag PAD X vertical θ/θ goniometer,

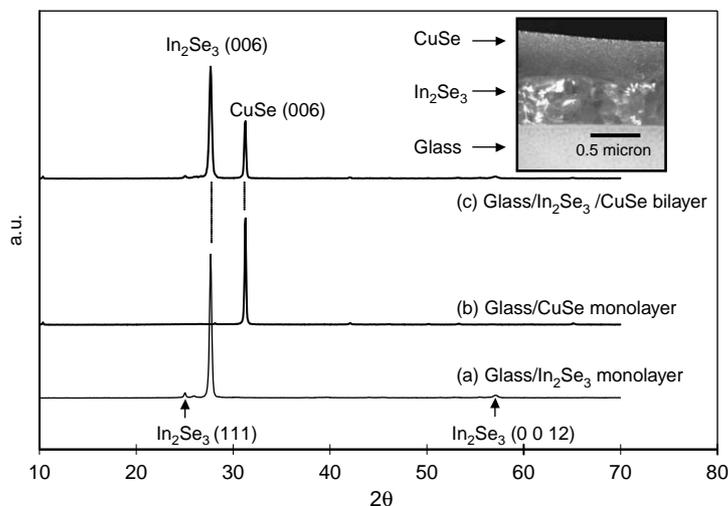


Fig. 1. Room temperature XRD scans and TEM micrographs of as-grown precursor films: (a) glass/ In_2Se_3 monolayer, (b) glass/CuSe monolayer, and (c) glass/ In_2Se_3 /CuSe bilayer.

a Buehler HDK 2.3 furnace, and an mBraun linear position sensitive detector (LPSD). The LPSD was centered at $29^\circ 2\theta$ and covered a 10° range (i.e. from 24 to 34°). In contrast to conventional X-ray point scanning detectors that perform the scanning step-by-step from lower to higher angles, the LPSD collects the XRD data simultaneously over the $10^\circ 2\theta$ window, dramatically shortening the data collection time. This permits in situ time-resolved studies of phase transformations, crystallization, and grain growth. The sample temperature was calibrated from a determination of the lattice expansion of silver powder dispersed on an identical glass substrate. The silver lattice parameters could be converted to accurate sample temperatures based on the data of Touloukian [11], to quantify the thermal offset between the heater strip and sample surface over the full temperature range of interest.

3. Results and discussion

3.1. Temperature ramp annealing

Temperature ramp annealing was used to investigate the phase evolution of the samples and to establish a suitable isothermal annealing temperature range. The glass/ In_2Se_3 /CuSe bilayer sample was first heated to 150°C at a rate of $10^\circ\text{C}/\text{min}$ and then X-ray diffraction data were collected during subsequent ramp heating ($5^\circ\text{C}/\text{min}$). Scans requiring ~ 1 min were taken at every 5°C increment, while the sample was heated from 150 to 350°C in a flowing He atmosphere. Fig. 2 demonstrates that the initial In_2Se_3 and CuSe phases are directly transformed to α -CuInSe₂ without any intermediate phases. CuInSe₂ begins to be detected at a temperature $\sim 250^\circ\text{C}$ and the reaction is almost complete at 310°C as evidenced by the lack of detection of In_2Se_3 and CuSe. The expected interfacial reaction pathway is

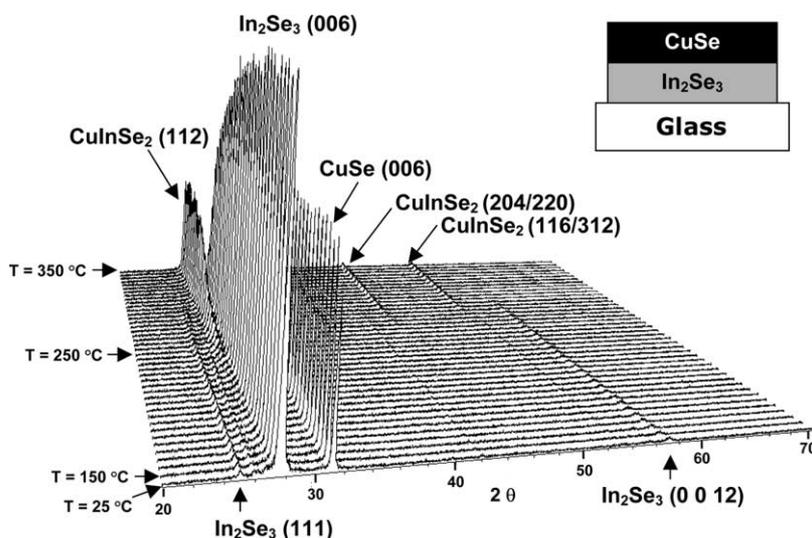
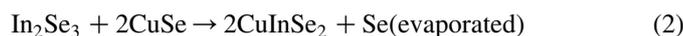


Fig. 2. In situ XRD scans during temperature ramp annealing ($10^\circ\text{C}/\text{min}$) of the glass/ In_2Se_3 /CuSe sample.

3.2. Isothermal annealing

Time-resolved, high temperature X-ray diffraction data were collected using a linear position sensitive detector (LPSD), while the bilayer glass/ In_2Se_3 /CuSe precursor films were maintained at a constant temperature in a He (flow rate ~ 100 sccm) atmosphere. The O_2 content of the outlet He gas was measured by an O_2 analyzer to be less than 0.1 ppm. In the isothermal experiment, three step temperature ramping was used to minimize heating time without temperature overshooting. First, the temperature was rapidly ramped at rate of $300^\circ\text{C}/\text{min}$ to a value of 20°C below the set point temperature, and then at rate of $200^\circ\text{C}/\text{min}$ to a value of 10°C below the set point temperature. Finally, the temperature was ramped to a set point at rate of $100^\circ\text{C}/\text{min}$ and then held to monitor the isothermal reaction. A set of experiments was performed with a range of set point temperature determined from the temperature ramp scan results shown in Fig. 2. The set point temperature was set so that the total isothermal holding time was much longer (i.e. several hours) than an individual scan. Scans were taken approximately every 35 s. It is noted that an individual scan time for the isothermal annealing experiment was much shorter (i.e. scan time of 30–120 s) than for the temperature ramp annealing (i.e. scan time of 5–10 min) to obtain acceptable time resolution. To complete the reaction, the temperature was elevated to 350°C and then maintained for about 12 min until only the α -CuInSe₂ phase was detected and the peak intensity remained constant (see, for example, the discontinuity in peak height after 1 h in Fig. 3). The temperature range for the isothermal experiments was from 230 to 290°C . The 2θ scan range (24 – 34°) for the isothermal experiments was selected to focus on the major peaks of the reactants and product, i.e. In_2Se_3 (006), CuSe (006) and α -CuInSe₂ (112).

Fig. 3 displays the time-resolved XRD data collected for the film isothermally reacted at 250°C . To obtain the fractional reaction (α), the integrated areas of the In_2Se_3 (006), CuSe (006), and CuInSe₂ (112) peaks were obtained from

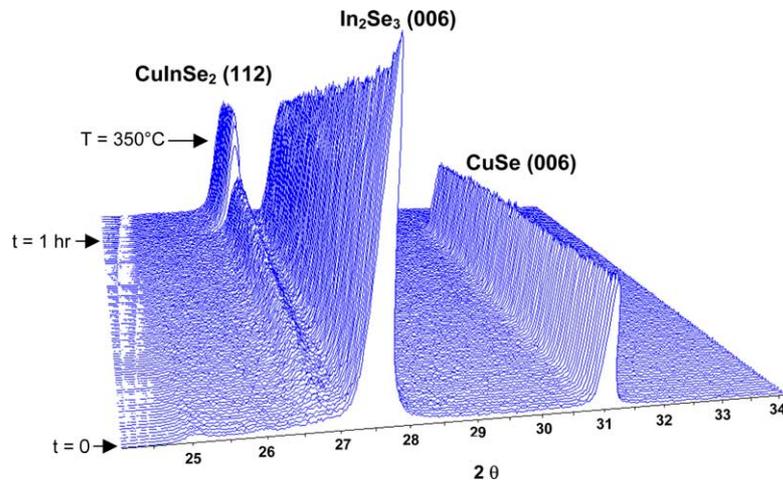


Fig. 3. In situ time-resolved XRD scans during isothermal annealing of the glass/ In_2Se_3 /CuSe precursor structure at 250°C .

the diffraction data using the JADE software [12]. These values were normalized assuming that the reactants were completely transformed to crystalline CuInSe_2 after each run, and that the texture of the CuInSe_2 does not appreciably change through the entire heating process.

3.3. Avrami model

The reaction kinetics in terms of activation energy and reaction order have been investigated using two solid-state reaction models, the ‘Avrami’ and ‘parabolic rate’ models. Analysis of solid-state reaction data using the Avrami model is commonly used for preliminary identification of the growth rate law. It has been shown that the method yields satisfactory fits to relevant experimental data [7,9,13,14]. Since this model is based on the nuclei growth and isotropic growth is assumed, the product regions are spherical. The transformation kinetics under isothermal reaction are described by

$$\alpha = 1 - \exp[-(kt)^n] \quad (3)$$

or equivalently, by

$$\ln[-\ln(1 - \alpha)] = n \ln t + n \ln k \quad (4)$$

where the fractional reaction α represents the fraction of reaction completed at time t , k is the kinetic rate constant, and n is the Avrami exponent. This analysis has been advocated by Hulbert [15], who showed that the Avrami exponent can vary between 0.5 and 1.5 in the case of one-dimensional, diffusion-controlled reactions. The value of n is close to 0.5 if the nucleation is instantaneous, and close to 1.5 if the nucleation rate is constant throughout the reaction. Fig. 4(a) displays the Avrami plots for the isothermal reaction of the precursor films at different temperatures. Even though data were taken only for $0.1 < \alpha < 0.95$ to minimize experimental error, the Avrami model expressed by Eq. (4) did not yield a satisfactory (i.e. linear) fit.

3.4. Parabolic model

The simple parabolic kinetic model [15] was developed based on a reaction between two solid materials with planar surfaces, and identical to the In_2Se_3 /CuSe precursor structure. This model is consistent with a physical process that requires a limiting reactant to diffuse across the product layer that initially formed at the interface of the two reactants. The product layer thickness increases with time to further decrease the diffusive

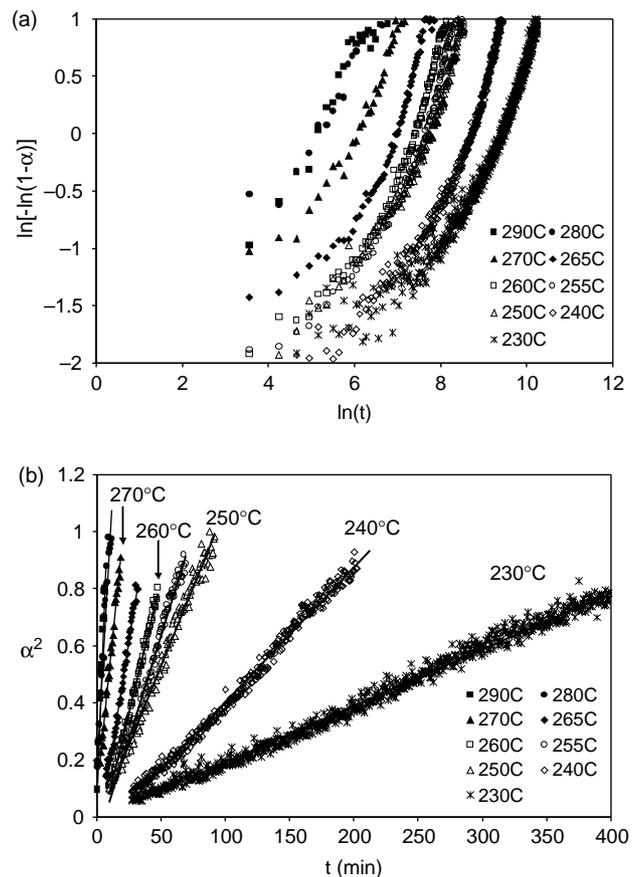


Fig. 4. (a) Avrami model plot, and (b) parabolic model plot.

flux of the limiting reactant. Assuming a uni-directional process, the reaction kinetics of parabolic model are described by

$$\alpha^2 = k_p t \quad (5)$$

where α is the fractional reaction, k_p is the parabolic rate constant including the diffusion coefficient of the migrating species, and t is the time. Fig. 4(b) shows the plot of α^2 vs. t for the same data set previously analyzed by the Avrami model. It is evident that the parabolic reaction model provides a much better fit to the data than the Avrami model over the entire set of isothermal temperatures (230–290 °C). It is thus concluded that the formation of α -CuInSe₂ in glass/In₂Se₃/CuSe bilayer precursor films is consistent with a one-dimensional diffusion controlled reaction pattern. The Arrhenius equation

$$k_p = A \exp\left(\frac{-E_a}{RT}\right) \quad (6)$$

was used to estimate the apparent activation energy E_a for the α -CuInSe₂ formation reaction in glass/In₂Se₃/CuSe bilayer precursor films. An activation energy of 162 (± 5) kJ/mol was estimated from the Arrhenius plot shown in Fig. 5. The estimated activation energy is very close to the value (~ 160 kJ/mol) suggested by Wolf et al. [8] for CIS formation from Cu/In/Se stacks using a Kissinger analysis of thin film calorimetric data.

4. Conclusions

Time-resolved, in situ high-temperature X-ray diffraction was successfully applied to investigate the reaction pathway and kinetics of polycrystalline α -CuInSe₂ formation from glass/In₂Se₃/CuSe bilayer precursor films. The qualitative reaction pathway observation during the temperature ramp annealing demonstrated that the stacked bilayer glass/In₂Se₃/CuSe structure directly transformed to α -CuInSe₂. Quantitative

kinetic analysis of X-ray diffraction data obtained during isothermal annealing fits the parabolic rate reaction model, which suggests that α -CuInSe₂ formation in a bilayer glass/In₂Se₃/CuSe precursor follows a one-dimensional diffusion controlled reaction pattern with an activation energy E_a of 162 (± 5) kJ/mol. The process likely involves the formation of a thin and planar α -CuInSe₂ layer at the In₂Se₃-CuSe interface. The reaction layer forms sufficiently rapidly that no nucleation incubation time is apparent. This layer serves to limit reactant diffusion and thus the rate of further reaction. Given the rapid diffusivity of Cu in α -CuInSe₂, it seems reasonable that continued growth of α -CuInSe₂ occurs by Cu diffusion across the barrier to the In₂Se₃- α -CuInSe₂ interface to react with In₂Se₃, which also requires transport of Se in the same direction. Of course, it is likely that some of the excess Se is also lost on the top side due to volatilization, as evidenced by the comparison of ICP results between precursor ([Se]/[Metal] ~ 1.2) and annealed CuInSe₂ ([Se]/[Metal] ~ 0.94).

Acknowledgements

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References

- [1] T. Gödecke, T. Haalboom, F. Ernst, Z. Metallkd. 91 (2000) 622.
- [2] T. Gödecke, T. Haalboom, F. Ernst, Z. Metallkd. 91 (2000) 635.
- [3] T. Gödecke, T. Haalboom, F. Ernst, Z. Metallkd. 91 (2000) 651.
- [4] S. Zweigart, D. Schmid, J. Kessler, H. Dittrich, H.W. Schock, J. Cryst. Growth 146 (1995) 233.
- [5] F.O. Adurodija, M.J. Carter, R. Hill, Solar Energy Mater. Sol. Cells 37 (1995) 203.
- [6] A. Katsui, T. Iwata, Thin Solid Films 347 (1999) 151.
- [7] A. Brummer, V. Honkimaki, P. Berwian, V. Probst, J. Palm, R. Hock, Thin Solid Films 437 (2003) 297.
- [8] D. Wolf, G. Müller, Thin Solid Films 361–362 (2000) 155.
- [9] S. Kim, W.K. Kim, E.A. Payzant, R.M. Kaczynski, R.D. Acher, S. Yoon, T.J. Anderson, O.D. Crisalle, S.S. Li, J. Vac. Sci. Technol., A 23 (2) (2005) 310.
- [10] B.J. Stanbery, S. Kincal, S. Kim, C.H. Chang, S.P. Ahrenkiel, G. Lippold, H. Nuemann, T.J. Anderson, O.D. Crisalle, J. Appl. Phys. 91 (2002) 3598.
- [11] Y.S. Touloukian, R.K. Kriby, R.E. Taylor, P.D. Desai, Thermophys. Properties Matter 12 (1977) 298.
- [12] JADE, A Program for Powder Diffraction Data Analysis, Version 6.5, Materials Data Inc., Livermore, CA, USA
- [13] C.H. Bamford, C.H. Bamford, C.F.H. Tipper, Reactions in the Solid State, Elsevier, Amsterdam, 1980.
- [14] K. Lu, M.L. Sui, J.H. Perepezko, B. Lanning, J. Mater. Res. 14 (1999) 771.
- [15] F. Hulbert, J. Br. Ceram. Soc. 6 (1969) 11.

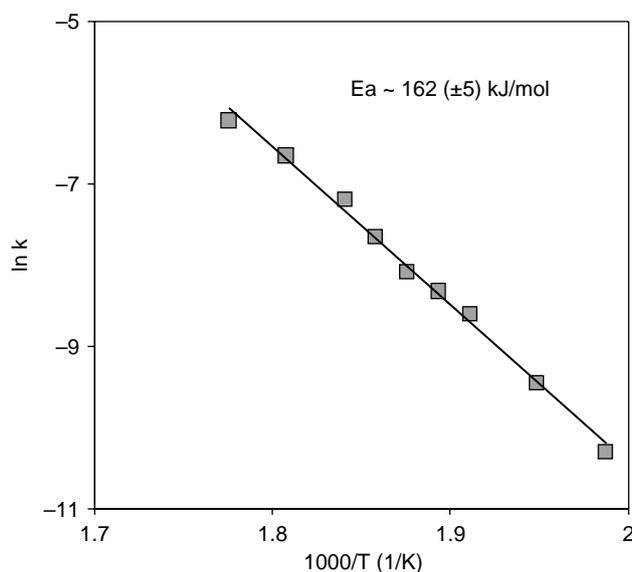


Fig. 5. Arrhenius plot of the parabolic rate constant.