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Activation energy of diffusion determined from a single in-situ neutron reflectometry experiment

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ABSTRACT

We present a new method for the determination of self-diffusivities in solids and the corresponding activation energy of diffusion using in-situ Neutron Reflectometry. In contrast to the classical ex-situ approach based on a sequence of isothermal measurements at different temperatures, the in-situ method allows one to work with a single experiment based on ramping the temperature with a constant rate. Our experiment demonstrates the success of the method for the model system of amorphous germanium. The activation energy of 2.2 eV and the absolute values of diffusivities achieved by the new method are in good agreement with the results of the classical approach, while a significantly lower amount of experimental time and samples are necessary. The presented method allows for an all-in-one type of experiment which can provide clearer and quicker results than similar methods using isothermal annealing procedures.

IMPACT STATEMENT

A new concept to determine diffusivities and the corresponding activation energy solely from a single measurement is presented which significantly lowers the experimental time and the number of samples used by classical methods.

ARTICLE HISTORY

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KEYWORDS

Neutron reflectometry; in-situ; material characterization; temperature ramp; activation energy; diffusion; amorphous germanium; isotope multilayer

1. Introduction

Self-diffusion in solids is a fundamental matter transport process important for synthesis [1] and tailoring of functional and structural properties of materials [2,3]. For example, microstructural re-arrangements like precipitation, crystallization, grain and layer growth, and plastic deformation as well as high temperature stability, semiconductor doping, and ion-conductivity in electrolytes and electrodes for batteries or fuel cells may be controlled by diffusion. Therefore, a basic understanding, an exact measurement of diffusivities and a further development of advanced experimental techniques for detection is of outermost importance.

The conventional and over several decades established procedure for carrying out tracer diffusion experiments in solids and the determination of the corresponding activation energy, is the following: In a first step, a small amount of a tracer (radioactive or rare stable isotope of an element) is deposited on the surface of the sample under investigation, e.g. ⁷³Ge on ^{nat}Ge (stable) or ⁷¹Ge on ^{nat}Ge (radioactive). Afterwards, isothermal annealing is carried out at an elevated temperature for a defined

time period in order to activate significant diffusion. The tracer is redistributed according to Fick's second law [2]. After cooling the sample to room temperature again the atoms become immobile and the redistributed tracer profile is frozen-in. The isotope depth profiles are analyzed ex-situ with methods like Secondary Ion Mass Spectrometry (SIMS) [4–8], Nuclear Reaction Analysis (NRA) [9], Neutron Reflectometry (NR) [10–24] or radiotracer sputter depth profiling [25].

The method of NR also allows to carry out *in-situ* investigations on kinetics and diffusion controlled process as shown for molten salts [26], organic layers [27–35], metals [11,12,24,36–38], oxides [39,40] and semiconductors [41].

NR in combination with isotope multilayers was established as an analytical method in order to measure tracer self-diffusivities in solids by isotope interdiffusion [11–21,23,24,39–42]. Here, the sample under investigation is prepared in form of isotope multilayers like [⁷³Ge/^{nat}Ge]. Due to the different coherent neutron scattering lengths of the isotopes, a Bragg peak is formed in the neutron reflectivity pattern. Self-diffusivities are

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determined by detecting the decay of the Bragg peak [41]. This method allows determining diffusion lengths on the nanoscale down to about 1 nm [15]. This is especially important for the investigation of amorphous [19] and nanostructured [21] materials due to their intrinsic metastability. In contrast to other methods, with advanced NR in form of ‘Focusing Reflectometry’ [43,44] it is possible to carry out diffusion measurements *in-situ* with a time-resolution of minutes as recently demonstrated for amorphous germanium by our group [41]. This enables a quasi-continuous detection of self-diffusivities directly during annealing, while cooling down is not necessary.

In order to determine the activation energy of diffusion in classical experiments, several distinct samples of a material under investigation have to be prepared and isothermally annealed, each at a different temperature. The diffusivity at a certain temperature is determined from the decrease of the Bragg peak in NR or more generally from the redistribution of the tracer concentration. The activation energy, Q , can be derived from a representation of the results in the form of an Arrhenius plot according to $\ln(D) = \ln(D_0) - Q / k_B \cdot (1 / T)$, where D_0 is the pre-exponential Factor, T the temperature and k_B the Boltzmann constant. This procedure requires several experiments at different temperatures (about 5–10 for new materials) and possibly several time steps for metastable materials, which is very time-consuming. The method of *in-situ* neutron reflectometry now basically allows the activation energy of self-diffusion to be determined in a single experiment as will be demonstrated in the present paper.

In such an experiment, the sample must be continuously heated starting from an initial temperature at which no diffusion takes place (e.g. at room temperature or another low temperature) with a constant heating rate R (e. g. 1 K / min). During heating up, measurements with neutron reflectometry (e.g. 1 reflectogram / min corresponding to 1 reflectogram / K) are carried out. The Bragg peak decreases continuously and the relative decrease in intensity can be evaluated. With the new approach, only one sample and one measurement are needed for a complete analysis.

Note that a combination of NR and temperature ramping was already suggested in [29] for the study of photoactive thin films, in [30,33,34] for depth profiling of chemical composition in organic layers, and in [37] for hydrogen absorption, however, without diffusivity determination.

In order to demonstrate the effectivity of the new method we use amorphous germanium as a model system, where recently isothermal measurements were carried out by NR and an activation energy of 2.1 eV

was determined [41]. The structure of amorphous germanium can be visualized as a fourfold coordinated continuous network of covalently bonded Ge atoms without long range order [45]. The crystallization temperature (random nucleation and growth) is around 450 °C depending on isothermal annealing times [46]. Annealing at temperatures below the crystallization limit may lead to diffusion controlled structural rearrangement processes and time-dependent diffusivities [41]. Short time pre-annealing of samples at 425°C, prior to the actual ramp diffusion experiments, will result in a metastable amorphous structure with constant diffusivities. Also atomic mixing of amorphous Ge during solid-phase epitaxial regrowth was investigated [47]. Germanium is used in this study as a model system due to the significantly different coherent neutron scattering lengths of ^{73}Ge and $^{\text{nat}}\text{Ge}$ giving rise to a large Bragg peak suitable for analysis. Further, germanium stays amorphous below 450°C and significant diffusion can be observed within the working range of our *in-situ* equipment.

The novelty of this work is the experimental demonstration of a concept to determine diffusivities and the corresponding activation energy of diffusion from a single experiment, which significantly lowers the experimental time and the number of samples used compared to classical methods.

2. Materials and methods

The diffusion experiments were carried out on [^{73}Ge (165 Å)/ $^{\text{nat}}\text{Ge}$ (165 Å)] $\times$ 10 multilayer structures which were produced by ion-beam sputter deposition [41], using a IBC 681 (Gatan) sputter coater equipped with two Penning sources. The coherent neutron scattering lengths are 5.02 fm for ^{73}Ge and 8.19 fm for $^{\text{nat}}\text{Ge}$, respectively. $^{\text{nat}}\text{Ge}$ layers were sputtered from a disc-shaped polycrystalline germanium target with a diameter of 2 cm (MaTecK, Germany), and ^{73}Ge layers were deposited from a corresponding ^{73}Ge enriched target (^{73}Ge enrichment > 99.3%, MaTecK, Germany) with a deposition rate of 4 nm/min. Both targets can be installed simultaneously in this setup and used successively without breaking the vacuum. Before each deposition, the targets were pre-sputtered to remove possible atmospheric contaminants. Sputtering was done using argon as a sputter gas at a base pressure below 5×10^{-7} mbar, an acceleration voltage of 5 kV and a beam current of 180 μA . As substrates (100) oriented, polished, unetched and nominally undoped Germanium wafers (CrysTec, Germany) were used. The as-deposited multilayers have an overall thickness of 330 nm. No additional heating was applied during deposition. The substrate temperature was not measured during

this sputter run but it is generally below 80 °C [48,49] due to the low impact energy of tens of eV for the deposited ions [50].

The in-situ NR measurements were realized with the Selene setup implemented at the time-of-flight reflectometer Amor located at SINQ (Paul Scherrer Institute, Villigen, Switzerland) [43,44]. For standard NR methods either angle (θ) or wavelength (λ) is kept fix and the other parameter is varied. The Selene setup allows to vary both at the same time by determination of the wavelength by time-of-flight, and the scattering angle with a position sensitive detector. The Selene wave guide provides a focused beam with a wider divergence. This reduces the measurement time considerably, for small scattering vectors by about an order of magnitude. The actual experimental arrangement allows to measure the reflected intensity continuously, while reflectivity patterns with sufficiently low statistical errors correspond to a counting time of 1–2 min.

Annealing was performed in a specially designed thermal annealing setup (AO 500, MBE-Komponenten GmbH, Germany) in argon gas. For the in-situ NR experiments the annealing setup was optimized for use in the neutron beam by equipping it with two sapphire windows for entrance and exit of the neutron beam. The temperature of the sample was recorded during the NR measurement by a PT100 thermocouple and controlled by a PID controller. The sample under investigation was pre-annealed at 425 °C for 5 min before the actual diffusion experiment in order to achieve a metastable state and time-independent diffusivities.

Grazing-Incidence X-ray Diffractometry (XRD) for structural characterization of a sample before and after pre-annealing at 425 °C for 5 min was carried out using a Panalytical Empyrean diffractometer ($\text{CuK}\alpha$, 40 keV, 40 mA, incidence angle $\alpha = 1^\circ$). The sample was X-ray amorphous. Crystallization of germanium takes place at 425 °C on an annealing time scale of several hours. For crystalline samples, Bragg peaks indexed as (111), (220), (311), (400) and (331) in (h k l) for the cubic diamond lattice are present, indicating random nucleation and growth taking place [41]. The program package OriginPro 2021 was used for numerical integration and graph plotting.

3. Results and discussion

Figure 1(a) shows the neutron reflectivity patterns of a multilayer sample in the pre-annealed state and after additional annealing during ramping with a rate of 1 K/min recorded in-situ by NR. The initial Bragg peak at about $0.022 \text{ \AA}^{-1}$ and the continuous decrease during annealing is clearly visible. In Figure 1(b) a contour

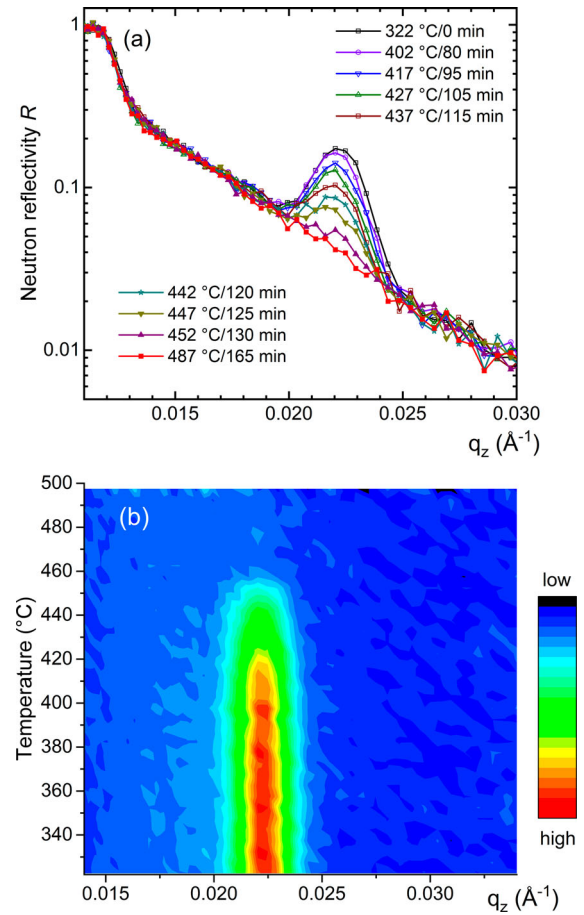


Figure 1. (a) Selected neutron reflectivity patterns recorded in-situ for a $[\text{}^{73}\text{Ge} (165 \text{ \AA})/\text{}^{\text{nat}}\text{Ge} (165 \text{ \AA})] \times 10$ multilayer sample during ramping the temperature from 322 °C to 500 °C with 1 K/min. The sample was pre-annealed at 425 °C for 5 min. Various time steps corresponding to temperature steps are indicated. The recording time of a single reflectivity pattern was 5 min. (b) Contour plot of the quantity $R \cdot q_z^4$ as a function of temperature and wave vector q_z (red: high relative intensity, green: middle relative intensity and blue: low relative intensity).

plot is given, illustrating the continuous decrease of the Bragg peak until complete vanishing. In Figure 2 the relative Bragg peak intensity I/I_0 is plotted as a function of annealing time, where I_0 is the intensity of the pre-annealed sample. The quantity I was determined by fitting a Bragg peak with a Gaussian function. Since during ramping each annealing time corresponds to a certain temperature, this quantity is also indicated. The experiment was done with a ramp of 1 K / min at a starting temperature of $T_0 = 322^\circ\text{C}$. The counting time for a single reflectivity pattern was (a) 2 min and (b) 5 min, respectively.

The relative intensity of the Bragg peak as a function of annealing time, t , as shown in Figure 2 is given by [17]

$$\frac{I}{I_0} = \exp\left(-\frac{8\pi^2}{d^2}\bar{D}(t)t\right) \quad (1)$$

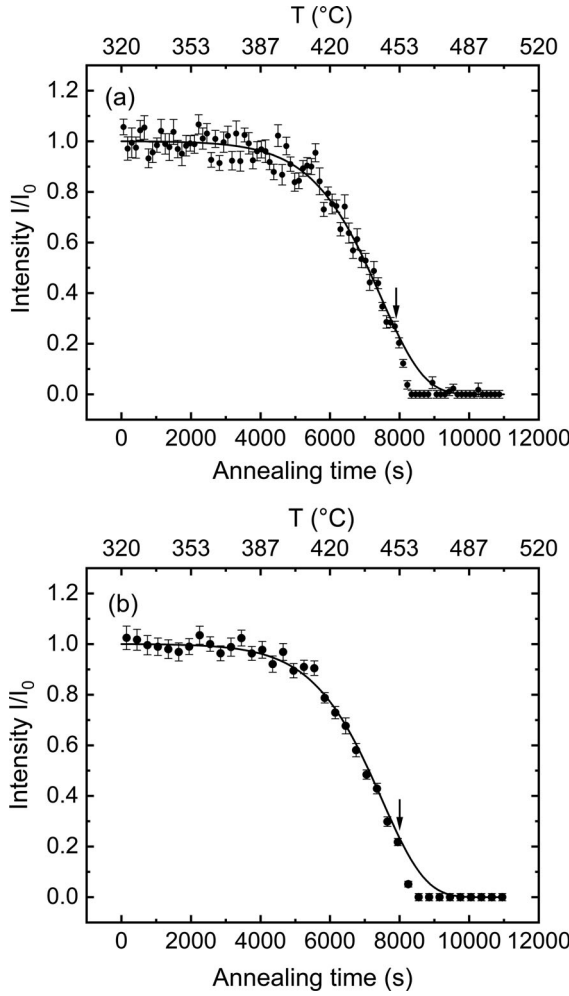


Figure 2. Integrated and normalized intensity of the Bragg peak, I/I_0 , as a function of annealing time with a ramp rate of $R = 1$ K/min and a starting temperature of $T_0 = 322^\circ\text{C}$. The corresponding temperature is also indicated. The counting time for a single reflectivity pattern was (a) 2 min and (b) 5 min, respectively. The expected onset of crystallization is marked by an arrow. The lines correspond to least-squares fits up to about 8000 s with equation (4).

where, $d = 33$ nm is the $^{73}\text{Ge}/^{\text{nat}}\text{Ge}$ bilayer thickness and $\bar{D}$ is the time averaged diffusivity. This quantity is given by

$$\bar{D}(t) = \frac{1}{t} \int_0^t D(t') dt' \quad (2)$$

where $D(t')$ is the instantaneous diffusivity that is defined as

$$D(t') = D_0 \exp\left(-\frac{Q}{k(T_0 + Rt')}\right). \quad (3)$$

Here, $T_0 = 322^\circ\text{C}$ is the starting temperature of the ramp, Q is the activation energy of diffusion, and D_0 is the pre-exponential factor. Combining equations (1–3)

we get

$$\frac{I}{I_0} = \exp\left(-\frac{8\pi^2}{d^2} \int_0^t D_0 \exp\left(-\frac{Q}{k(T_0 + Rt')}\right) dt'\right). \quad (4)$$

The experimentally observed modification of the relative Bragg peak intensity in Figure 2 is now fitted by equation (4) with simultaneous numerical integration. The quantities Q and D_0 are the only free fit parameters. The results are indicated in Figure 2 by lines. Note that fitting was carried out for data corresponding to time intervals up to values of about 8000 s as indicated by an arrow. For higher times we observe a deviation between fit and data. This is due to the fact that within this temperature/time domain crystallization sets in, which might accelerate diffusion. Investigations with X-ray diffractometry on amorphous samples annealed at about 450°C revealed that crystallization starts for annealing times above 200 s, while at 425°C a longer time of 1500 s is necessary (Figure 3). This is in agreement to the findings of Figure 2.

Note that the results of Figure 2 can be subdivided into two temperature regions: the region of almost constant intensity (up to about 390°C corresponding to 4000 s) and the region of strong decay. During the ramp experiment, measurable diffusion becomes visible at this transition region as a consequence of the exponential increase of diffusivities as a function of temperature (equation (4)). Below this temperature annealing is not sufficient to induce measureable isotope intermixing due to too low diffusivities, while above that temperature diffusion is heavily accelerated leading to the strong decrease. The activation energy of diffusion (Q) determines the slope of the decay and the pre-exponential factor (D_0) affects the temperature value at which the strong decay starts.

As a result of fitting we get from Figure 2(a) $Q = 2.14^{+0.25}_{-0.20}$ eV and $D_0 = 1.25^{+7.8}_{-1.2} \times 10^{-5} \text{ m}^2/\text{s}$. Errors correspond to a 10% increase of χ^2 of the best fit with respect to the fitted parameter only. Further we obtain from Figure 2(b) $Q = 2.29^{+0.17}_{-0.15}$ eV and $D_0 = 1.55^{+18.4}_{-1.3} \times 10^{-4} \text{ m}^2/\text{s}$. Both quantities are identical within error limits or close to each other. The relatively high errors are due to the fact that both quantities are correlated. As a consequence, with our new method it is possible to determine the activation energy of diffusion within an error range of about 10–15%. Nevertheless, the activation energies obtained are also in excellent agreement to the value of (2.11 ± 0.12) eV recently obtained by the classical method using isothermal annealing [41].

In Figure 4 the diffusivities calculated from Q and D_0 using the Arrhenius equation are displayed as a red

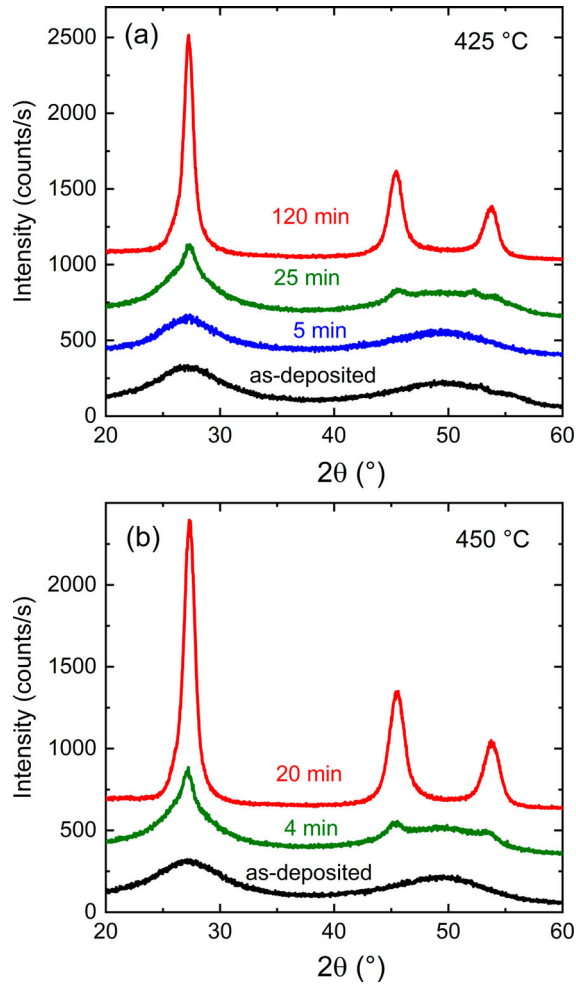


Figure 3. Grazing incidence X-ray diffraction patterns of 240 nm thin amorphous Ge films at (a) 425°C and (b) 450°C for different annealing times. The patterns are shifted in intensity along the ordinate for clarity.

and blue straight line. Note that the temperature range, where diffusivities are shown, results from the range where in Figure 2 a modification of the relative intensity is visible.

Also shown in Figure 4 are the results of the classical approach (dots), where a sequence of isothermal measurements on a number of five germanium samples were investigated. This approach needs much more experimental effort, because the determination of each diffusivity value consumed a Ge isotope ML sample. Here, also a good agreement between the absolute values of diffusivities is given for both methods.

The fact that with the NR technique reliable self-diffusivities in solids can be determined is confirmed by a comparison to other established ex-situ techniques like SIMS. Examples can be found for crystalline Ge [16], Si [42] and LiNbO₃ [20,22]. Further, Li permeabilities through thin amorphous Si layers were determined

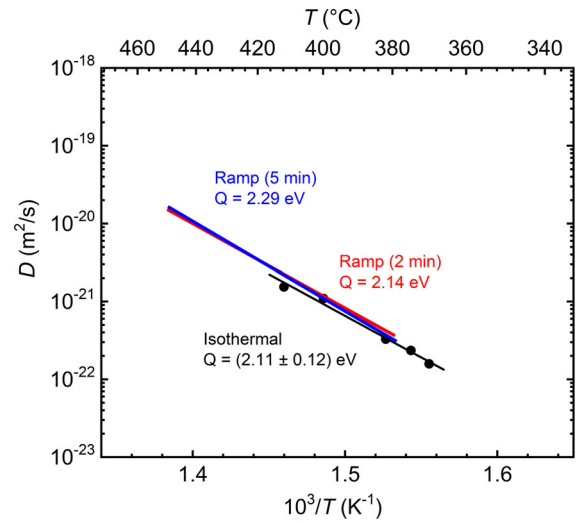


Figure 4. Tracer self-diffusivities of amorphous germanium pre-annealed at 425°C for 5 min plotted against the reciprocal temperature as obtained in the present work using the ramping method. Also shown are literature data measured on the same type of samples using the classical isothermal method (dots) [41].

in-situ by NR and ex-situ by SIMS in direct comparison and agreement [40].

In order to avoid crystallization during the measurement, it is planned for future experiments to reduce the ramp rate to lower values, which should result in prolonged annealing at lower temperatures and a decrease of the Bragg peak before crystallization sets in. A discussion of a possible diffusion mechanism can be found in [41].

4. Conclusions

In-situ neutron reflectometry can be used to determine self-diffusivities in solids and the corresponding activation energy within a single experiment based on ramping the temperature with a constant rate. Here, the reflectivity of an amorphous Ge isotope multilayer was measured in-situ during ramping with a rate of 1 K /min between 322°C and 500°C. An activation energy for self-diffusion in amorphous Ge of 2.2 eV was obtained. The feasibility and reliability of the new method was convincingly demonstrated by the comparison between the results of the present study with those of the classical approach based on a sequence of isothermal measurements on a number of five germanium samples. The diffusivities achieved are in excellent agreement, while a significantly lower amount of experimental time and number of samples are necessary using the new method. The new methodology may also be sensitive on other materials processes such as crystallization if the involved process influences the diffusivity.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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