Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Impact of surface roughness on tracer depth profiling and its implications for ^{109}Cd and ^{65}Zn diffusion experiments in solar-grade Cu(In,Ga)Se$_2$ layers

T. Eschen, K. Hiepko, J. Bastek, N.A. Stolwijk*

Institut für Materialphysik, Universität Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany

ABSTRACT

It is shown by numerical simulation that surface roughness affects the measurement of diffusion profiles by means of serial sectioning techniques. This problem arises in radiotracer diffusion studies of Cd and Zn in thin-film solar-grade Cu(In,Ga)Se$_2$, which exhibits an appreciable surface roughness due to the special manufacturing process of the polycrystalline layer structure. We find that in unfavorable cases the experimentally determined diffusivity can be significantly higher than the true diffusion coefficient D. This discrepancy appears to increase with the ratio of the surface roughness R_{rms} to the average penetration depth $\sqrt{2Dt}$ attained after a diffusion time t. It can be concluded, however, that the employed ion-beam sputtering technique, which involves rotation of the Cu(In,Ga)Se$_2$ diffusion sample, usually leads to experimental errors of ∼10% or less. The results of this study may be also relevant to other depth profiling techniques such as secondary ion mass spectrometry.

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1. Introduction

A widely used and accurate method for determining diffusion coefficients in solid state materials is the radiotracer technique. The experimental procedures involved here are consecutively: (i) the deposition of a suitable radioisotope on the flat (front) surface of a material sample, (ii) a diffusion treatment at a fixed elevated temperature (T) for an appropriate time length (t), (iii) serial sectioning of the sample parallel to the front surface, and (iv) detection of the radioactivity in each section. A plot of the measured specific activity (recorded decay events per unit of mass or volume) versus distance from the front surface eventually leads to a radiotracer depth profile. Depending on the boundary conditions, the shape of the diffusion profile usually corresponds either to a Gaussian or to a complementary error function (erfc) [1]. Least-squares fitting of the measured profile with either of these functions yields the diffusion coefficient (D).

Sectioning can be done by different techniques depending both on the mechanical properties of the material to be investigated and the expected depth of the diffusion profile. Nowadays, sectioning is most frequently performed by microtome cutting, precision grinding or ion-beam sputtering. For brittle materials such as

semiconductor crystals the latter two methods cover different depth scales. Precision grinding is a suitable technique for section thicknesses on the order of ∼1 μm or larger and total tracer penetration depths of at least 10 μm. On the other hand, ion-beam sputtering (IBS) provides the optimal depth resolution for sections of roughly 30–100 nm thickness and diffusion profiles extending to depth ranges from 400 nm to 2 μm in total.

In the above procedure it is implicitly assumed that the front surface of the diffusion sample may be considered as being smooth. In practice, this means that the root-mean-square surface roughness (R_{rms}) should be much smaller than the thickness of a typical section. A more rigorous formulation requires that R_{rms} must be negligibly small with respect to the mean penetration depth $\bar{x}_p$, which for a constant diffusivity D is given by

$$\bar{x}_p \equiv \langle x^2 \rangle^{1/2} = \sqrt{2Dt}. \qquad (1)$$

For deep diffusion profiles, to be resolved by mechanical sectioning, the condition $R_{rms} \ll \bar{x}_p$ is usually automatically fulfilled. In other cases, mostly involving ion-beam sputtering, this condition can be met by additional polishing of the sample to the required surface finish. However, difficulties arise if such polishing treatments are not possible or less successful.

Recently, problems due to surface roughness were encountered in diffusion studies carried out at our laboratory on thin film solar cell structures based on Cu(In,Ga)Se$_2$ (CIGSe). Specifically,

* Corresponding author. Tel.: +49 2518339013.

the experiments concerned the diffusion of Fe, Cd and Zn, which was monitored by suitable radiotracers of these impurity elements [2–4]. CIGSe layers are typically 2 μm thick and their front surface is usually characterized by R_{rms} values ranging from 100 to 220 nm. This substantial roughness arises from the thin film manufacturing process and the polycrystalline structure of the CIGSe layer [5]. Polishing treatments, either mechanical or chemical, are difficult to apply due to the small width of the CIGSe layer, its defect structure and the observed stress-induced surface warpage of the sample. Thus, it was decided to perform the diffusion experiments including IBS sectioning with the as-grown surface roughness [2–4] and to take the associated deviation from the ideal boundary conditions for granted.

For Cd and Zn diffusion in CIGSe, indeed some remarkable features were reported. In particular, it was found that for a fixed temperature the (apparent) diffusion coefficient deduced from the radiotracer profiles after short-term annealing differed from the corresponding diffusivity after long-term treatments. Furthermore, some deviations from the standard Gaussian- or erfc-type profiles were observed in regions close to the surface. Motivated by these findings, this work examines the influence of rough surfaces in radiotracer diffusion experiments with the aid of numerical calculations. Specifically, within a finite-difference framework we follow the evolution of the depth profile and the diffusion coefficient deduced there from as a function of annealing time at constant temperature. The results are compared with experimental data for Cd and Zn in CIGSe. Finally, some useful conclusions for future studies will be drawn.

2. Numerical calculations

2.1. Basic equations and analytical solutions

Diffusion processes can be usually analyzed on the basis of Fick's second law, which describes the relation between the particle concentration $C = C(x, y, z)$ at the location x, y, z after a diffusion time t:

$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C). \tag{2}$$

In the case of a constant diffusion coefficient D and one-dimensional geometry (with diffusion distance x) this equation can be solved analytically for certain simple initial and boundary conditions. A standard solution is the complementary error function [1,6]

$$C(x) = C_0 \mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right), \tag{3}$$

which holds for a constant concentration C_0 of the diffusing species at the surface at $x = 0$. This situation requires that the amount of tracer atoms per unit area M_0 initially deposited at the front surface is large enough to maintain such *constant source condition* during the entire diffusion treatment. For impurity elements, C_0 may be conceived as the equilibrium concentration under the given conditions. Another common solution is the Gaussian function [1,6]

$$C(x) = C_0(t) \exp\left(-\frac{x^2}{4Dt}\right), \tag{4}$$

which describes the diffusion profile for a thin-film diffusion source. Under *these instantaneous source conditions* virtually all tracer atoms take part in the diffusion process from the onset of annealing. As a consequence $C_0(t) = M_0/\sqrt{\pi Dt}$ decreases with increasing diffusion time.

Whether an erfc- or Gaussian-type profile is observed for a given diffusion source of strength M_0, generally depends on the tracer element of interest, the diffusion temperature (T), and the duration

Fig. 1. Two-dimensional schematic of a material sample with a rough surface.

of annealing. In sufficiently early stages of any diffusion process, the constant source condition *in principle* prevails, since then the total amount of diffusing substance [1,6]

$$M(t) = 2C_0\sqrt{Dt/\pi} \tag{5}$$

is still much less than M_0. Introducing a critical time t_c defined as $M(t_c) = M_0$, it may be expected that a Gaussian-type penetration profile develops for times $t \gg t_c$. This implies that for intermediate times the experimental profile may be a 'mixed form' between the Gaussian and erfc shape [6,7]. Such a special solution of the diffusion equation is given by

$$C(x) = \frac{1}{2} C_0 \left[\mathrm{erf}\left(\frac{w_s - x}{2\sqrt{Dt}}\right) + \mathrm{erf}\left(\frac{w_s + x}{2\sqrt{Dt}}\right) \right], \tag{6}$$

where w_s denotes the width of the diffusion source layer having the same diffusivity D as the substrate sample material [6]. For $\overline{x}_p \gg w_s$, Eq. (6) converges to the Gaussian function with $C_0(t) = w_s C_0/\sqrt{\pi Dt}$.

By fitting the more appropriate function among Eqs. (3), (4) and (6) to the experimental depth profile one can determine the diffusion coefficient D_{app}. However, these solutions of Fick's second law are based on the assumption that the host material is not only fully homogeneous but also has semi-infinite geometry and an ideally smooth surface. Obviously, these conditions are not ideally fulfilled in practice and therefore the D_{app} values obtained are only approximations to the true diffusivities D.

2.2. Computing scheme for rough surfaces

2.2.1. Representation of surface roughness

Fick's second law represented by Eq. (2) is a partial differential equation (PDE), which in general cannot be solved analytically. Therefore, to investigate the effect of a rough surface we find numeric solutions to this equation by using PROMIS [8], a software framework that is specialized on solving PDEs. This framework offers an interface which can be used to specify the equation system, the simulation area and the pertaining boundary conditions. The simulation area naturally has one temporal dimension but up to two spatial dimensions.

As a first step towards modeling the CIGSe samples used in the diffusion experiments we simplify the problem by reducing the three-dimensional (3D) sample geometry to its two-dimensional (2D) analog. The rough surface is mimicked by a symmetrical saw-tooth pattern composed of periodically repeated equal-sided triangular spikes, as shown in Fig. 1. Each spike has a base width of 2 μm, roughly corresponding to the grain sizes of solar-grade CIGSe layers.

The complexity of the calculation is further reduced by the assumption that the sample has an infinite extension in the *y*-direction parallel to the surface. With this setup the sample has no side-boundaries (oriented along the *x*-direction) and consists of a recurring pattern of unit cells with a height of 10 μm. The smallest unit cell involves a half-spike at the surface, as shown in Fig. 2. With suitably chosen boundary conditions, the solution of Eq. (2) for the half-spike cell is representative to the solution of the full sample, which minimizes the necessary computing time.