

# Diffusion of Au in ZnSe and its dependence on crystal quality

J. Slotte,<sup>a)</sup> R. Salonen, T. Ahlgren, E. Rauhala, J. Keinonen, and J. Räisänen<sup>b)</sup>  
*Accelerator Laboratory, University of Helsinki, P.O. Box 43, FIN-00014 University of Helsinki, Finland*

P. Uusimaa, A. Salokatve, and M. Pessa  
*Department of Physics, Tampere University of Technology, P. O. Box 692, FIN-33101 Tampere, Finland*

A. Laakso  
*Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, FIN-02015 HUT, Finland*

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Diffusion of gold in zinc selenide has been studied by using a  $^{12}\text{C}$  and  $^4\text{He}$  ion backscattering technique. The samples were thin films grown by molecular beam epitaxy on bulk GaAs (100) substrates and on GaAs (100) epitaxial layers followed by evaporation of gold and annealing in the temperature range 400–800 °C. The surface properties of the samples were studied with scanning electron microscopy and atomic force microscopy. The crystal quality of the samples was studied with  $^4\text{He}$  ion channeling. The gold diffusion was found to depend significantly on the crystal quality of the ZnSe. An empirical model for calculating the diffusion coefficient for different crystal quality ZnSe is presented. © 1999 American Institute of Physics. [S0021-8979(99)06002-8]

## I. INTRODUCTION

Gold is a widely used metal for ohmic contacts on compound semiconductor devices. When making the ohmic contacts the thermal stability of a gold/semiconductor interface is of prime importance. In this article, we study the diffusion of gold into the wide-gap semiconductor ZnSe which is used for green-blue laser diodes.

The electrical properties of Au/ZnSe contacts have been extensively studied, for example, in Refs. 1–5. In some of these studies indiffusion of gold and outdiffusion of zinc and selenium are reported, but no quantitative data for the diffusion in this material system are available in the literature. In this article we report the activation energy and pre-exponential factor for the diffusion of gold in ZnSe. We have found that the diffusion of gold in ZnSe depends on the crystal quality of the ZnSe lattice and we present an empirical model which accounts for this crystal quality dependence.

A common phenomenon for semiconductors with thin metal films on top is the formation of grains on the sample surface and even on the metal/semiconductor interface during the annealing. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were therefore used for studying sample surface properties. The effect of the surface properties on the Rutherford backscattering spectrometry (RBS) measurements was also taken into account.

## II. EXPERIMENT

Three series of unintentionally doped n-type ZnSe were grown at Tampere University of Technology. The first set was grown on bulk p-GaAs (100) substrates (labeled I), and the second and third sets were grown on epitaxial p-GaAs

buffer layers (labeled II and III). The growth temperature and the beam pressure ratio (Se:Zn) of all the layers were 290 °C and 2.0–2.5, respectively. The thicknesses of the ZnSe layers were 1.4–2.0  $\mu\text{m}$  causing them to be almost completely relaxed. The lattice relaxation was confirmed by x-ray diffraction measurement of each sample. After growth the samples were immediately transferred to an e-beam vacuum evaporator where a 70 nm thick gold layer was deposited onto sample series I, a 100 nm thick gold layer onto sample series II and a 10 nm thick gold layer onto sample series III.

A few of the samples were backsputtered with argon atoms prior to metal deposition. This was done in order to study if the backsputtering, which is often used to clean the samples, would have an effect on the diffusion properties.

The annealing was carried out in a quartz-tube furnace in argon atmosphere at a pressure of approximately 660 Torr. The samples were annealed for 30 min–27 h in the temperature range 400–800 °C. The annealing temperatures were measured with a calibrated Chromel-Alumel thermocouple in close contact with the samples.

The depth profiles of sample series III were determined by 2.5 MeV  $^4\text{He}$  ion backscattering with a 2.5 MV Van de Graaff accelerator at the accelerator laboratory. The scattering angle was 170° and the angle of incidence was 5°. Concentration profiles for sample series I and II could not be obtained with 2.5 MeV  $^4\text{He}$  ion backscattering since the gold had diffused 300–800 nm into the ZnSe and the signal from the diffused gold thus overlapped the signal from the ZnSe. The depth profiles of sample series I and II were, therefore, determined by 15 MeV  $^{12}\text{C}$  ion backscattering with the accelerator laboratory's 5 MV tandem accelerator EGP-10-II. The scattering angle in these measurements was 165° and the angle of incidence was 7°. The depth profiles were extracted from the measured backscattering spectra with the aid of computer program GISA 3.99.<sup>6</sup> GISA is designed for the analysis of RBS spectra; it calculates theoretical spectra

<sup>a)</sup>Corresponding author; electronic mail: cjslotte@kruuna.helsinki.fi

<sup>b)</sup>Permanent address: Department of Physics, University of Jyväskylä, P.O. Box 35, FIN-40351 Jyväskylä, Finland.

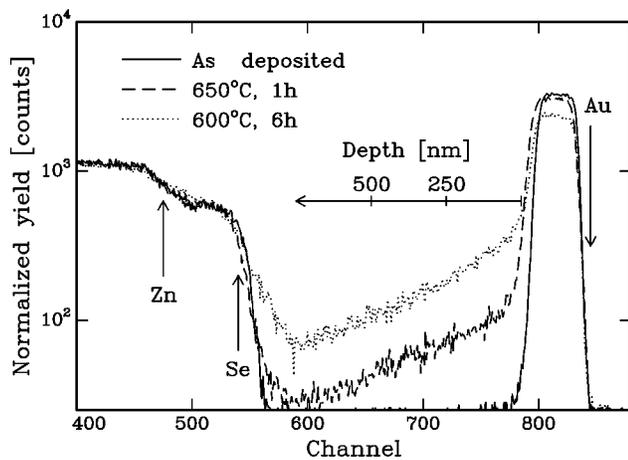


FIG. 1. Examples of  $^{12}\text{C}$  15 MeV RBS spectra of sample series II (gold layer thickness 100 nm), with an approximate depth scale. The scattering angle was  $165^\circ$  and the angle of incidence  $7^\circ$ .

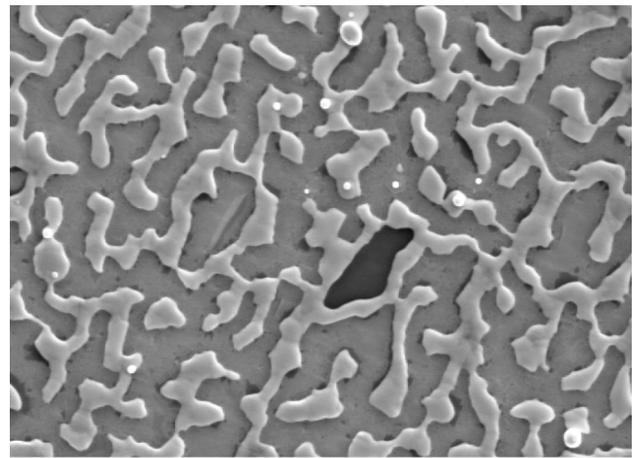


FIG. 2. Typical secondary electron SEM micrograph ( $45\ \mu\text{m} \times 30\ \mu\text{m}$ ) of a sample surface. The sample (series II) was annealed for 30 min at  $650^\circ\text{C}$ .

which are compared to measured ones. Experimental parameters, such as detector resolution, are included in the theoretical calculations. Nonconstant depth profiles can be deduced from experimental RBS spectra by iteration. Examples of measured backscattering spectra can be seen in Fig. 1.

Since the diffusion properties can depend on the crystal quality, the quality of the three sample series were studied with 2 MeV  $^4\text{He}$  ion channeling. Ion channeling is commonly used to determine the crystal quality of samples. This is done by comparing the backscattering yield in the random direction to the yield in a channeled direction. The minimum yield is defined as the ratio of the channeled yield to the random yield just below the sample surface, the smaller the minimum yield the better the crystal quality. In our experiments these yields were taken from a depth interval 100–150 nm below the surface. For these measurements the gold layer was removed chemically from the samples. The minimum yield for the  $\langle 100 \rangle$  channel was 8.2% of the random yield for sample series I, 7.1% for sample series II and 5.4% for sample series III. The uncertainty in these values was 5%.

In several studies of ohmic contacts on compound semiconductors grain formation at the contact surface<sup>7–12</sup> and on the metal/semiconductor interface<sup>4</sup> has been reported. As the formation of grains may affect the RBS spectra<sup>13,14</sup> we studied the surface properties of the annealed samples with SEM and AFM. The SEM micrographs and AFM images revealed grains on the annealed sample surfaces, as can be seen in Fig. 2. By monitoring the backscattered electrons in the SEM study we could conclude that the grains consisted mainly of gold. However, a RBS microbeam study<sup>15</sup> also showed some zinc in the grains. The grain size varied from 1 to 3  $\mu\text{m}$  on sample series I and II and was on average 0.5  $\mu\text{m}$  on sample series III. The AFM studies showed that the average grain height was 150 nm on sample series I and II and 40 nm on sample series III. The grains covered up to 40% of the sample surfaces.

### III. DATA ANALYSIS

#### A. Modeling of RBS spectra

The topographical information of the sample surfaces obtained from the AFM measurements was used to calculate the subsequent theoretical RBS spectrum. These calculations were done with a  $^4\text{He}$  ion beam in order to be comparable with He micro- and macrobeam measurements.<sup>15</sup> A comparison between the measured RBS spectrum of an annealed sample and a calculated RBS spectrum can be seen in Fig. 3. The calculated RBS spectrum includes signals from the remaining gold layer and from the grains. It does not include signals from the diffused gold. As can be seen from Fig. 3 the surface properties do not affect the signal from the diffused gold below 100 nm. This conclusion was verified by performing a RBS microbeam measurement from a grain free area of the surface.

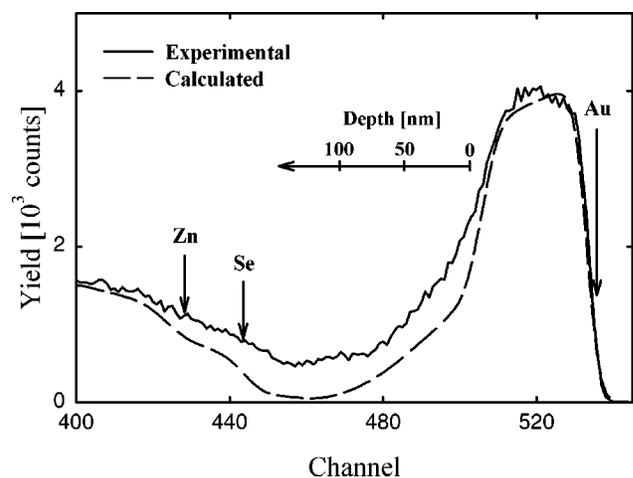


FIG. 3. Comparison between measured and calculated RBS spectra. The experimental spectrum was measured with a  $^4\text{He}$  2 MeV beam, the scattering angle was  $170^\circ$  and the angle of incidence  $5^\circ$ . The sample (series II) was annealed for 30 min in  $650^\circ\text{C}$ . An approximated depth scale for the diffused gold is indicated.

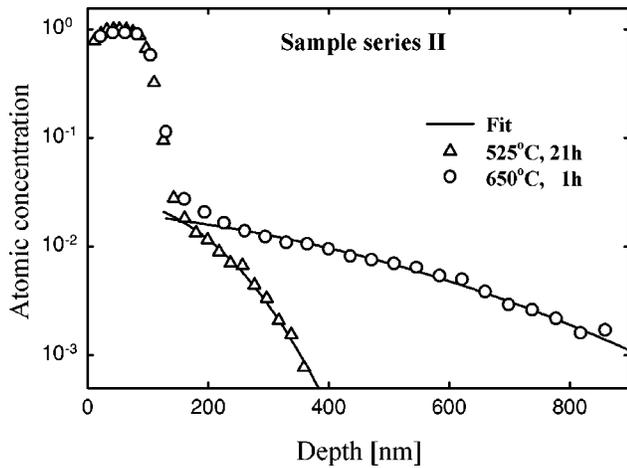


FIG. 4. Examples of least squares fits to depth profiles. The samples (series II) were annealed at 650 °C for 1 h and 525 °C for 21 h.

**B. Calculation of the diffusion coefficients**

Since diffusion can be concentration dependent or independent, we used the Boltzmann-Matano<sup>16</sup> method to study the concentration dependence of the diffusion coefficient,

$$D_{C=C_1} = -\frac{1}{2t} \frac{dx}{dC} \int_0^{C_1} x dC. \tag{1}$$

These calculations showed no concentration dependence of the diffusion coefficient. A concentration independent diffusion model which is governed by the differential equation of diffusion,<sup>16</sup>

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \tag{2}$$

was therefore used to determine the diffusion coefficients. In Eqs. (1) and (2), *C* is the concentration, *D* the diffusion coefficient, *t* the time and *x* the depth. The coefficients were calculated by least squares fitting of the analytical solution of the diffusion equation for an infinite diffusion source and an infinite medium,<sup>16</sup>

$$C(x,t) = \frac{1}{2} C_0 \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right), \tag{3}$$

to the experimental depth profiles. In Eq. (3) *erfc*(*x*) is the complementary error function. The fitting was done at depths 100 nm below the Au/ZnSe interface and beyond to avoid influence from the surface properties. Examples of such fits can be seen in Fig. 4.

**IV. RESULTS AND DISCUSSION**

The activation energies and pre-exponential factors for the diffusion of gold in ZnSe for the different sample series were calculated from the Arrhenius plots *log*(*D*) vs 1/*T* (inverse annealing temperature); see the solid lines in Fig. 5. The activation energies were 1.5, 1.6, and 1.8 eV for sample series I, II and III, respectively, and the corresponding pre-exponential factors were 2.3 × 10<sup>10</sup>, 4.8 × 10<sup>9</sup> and 5.7 × 10<sup>8</sup> nm<sup>2</sup>/s. It should be noted that we were not able to

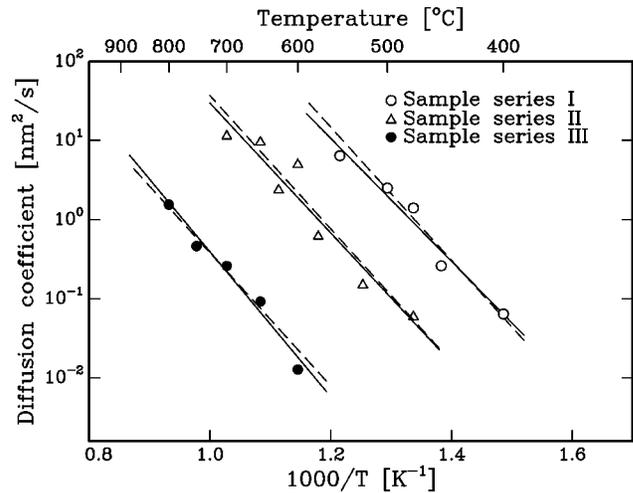


FIG. 5. Arrhenius plot of the diffusion coefficients for the three sample series. The solid lines are linear fits and the dashed lines are fits of Eq. (4) to the experimental data.

determine the diffusion coefficients for the samples that had been backspattered prior to metal deposition, since anomalous RBS spectra were obtained. However, it is clear that the backspattering both enhances and distorts the diffusion properties.

As can be seen from Fig. 5 the diffusion coefficient increases with increasing backscattering minimum yield, i.e., the better the crystal quality is, the smaller the diffusion coefficient. We find that the following empirical model can be used for calculating the diffusion coefficients in different crystal quality samples as a function of the backscattering minimum yield:

$$D = A e^{B\chi - E_a/(kT)}. \tag{4}$$

In Eq. (4) *A*, *B* and *E<sub>a</sub>* are fitting parameters with values of 48.5 nm<sup>2</sup>/s and 2.69 and 1.67 eV, respectively. *χ* is the backscattering minimum yield in %, *T* is the temperature in kelvin and *k* is the Boltzmann constant. The fitting of this model to the calculated diffusion coefficients was done in a least squares sense. The result of the fitting can be seen in Fig. 5 as the dashed lines.

A possible explanation for the dependence on crystal quality of the diffusion is the difference in defect concentration in the three sample series, as seen by the channeling measurements. The channeling measurements indicate the presence of Zn and/or Se interstitials, dislocations and/or stacking faults, but they do not indicate anything about the possible vacancies present in the material. The diffusion of impurities has been shown to depend strongly on both extended and point defects.<sup>17</sup> For sample series I the growth of the ZnSe layer was done directly on the GaAs layer. The lattice constant mismatch of these structures may create dislocations, stacking faults and voids. Since the pre-exponential factor is proportional to the diffusion jump frequency, diffusion along dislocations or stacking faults could explain the higher value of the pre-exponential factor for sample series I. The use of an epitaxial buffer layer has been shown to reduce the formation of these defects.<sup>18</sup> The difference in the gold diffusivity in sample series II and III can

possibly be explained by the difference in the Se to Zn beam pressure ratios during growth, 2.0 and 2.5 for sample series II and III, respectively. This difference can result in higher defect concentration in sample series II and thus higher diffusivity. The concentration of defects, such as vacancies or interstitials, in the samples can be assumed to be constant throughout the relaxed ZnSe, since the defects have been formed during growth. The Boltzmann-Matano calculations and the good agreement of the complementary error function fit with the experimental depth profiles clearly show that the gold diffusion in ZnSe is concentration independent. Hence, the defect concentration does not depend on the gold concentration.

We note in passing that according to an earlier report<sup>5</sup> the formation of ohmic contacts requires annealing of Au/ZnSe heterostructures at 350 °C for 30–45 min. This translates into a diffusion length of 10 nm for sample series I, as deduced from the present study. At temperatures below 250 °C the diffusion would be negligible.

## V. CONCLUSIONS

To summarize, we have studied thermal stability of gold contacts on ZnSe grown on both bulk GaAs and epitaxially grown GaAs. The samples were subjected to annealing in argon atmosphere in the temperature range of 400–800 °C. Scanning electron microscopy and atomic force microscopy studies showed grain formation on the sample surfaces. The effect of surface properties on the backscattering measurements was studied and was found to be negligible 100 nm below the Au/ZnSe interface and beyond. The diffusion coefficients for gold diffusion in ZnSe were deduced from the depth profiles by the use of a concentration independent diffusion model. The diffusion coefficient was found to depend on the crystal quality of the ZnSe and an empirical model for calculating the diffusion coefficient in samples with different crystal quality was presented.

## ACKNOWLEDGMENT

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