

Diffusion of Pt in molecular beam epitaxy grown ZnSe

J. Slotte,^{a)} R. Salonen, T. Ahlgren, J. Räisänen, and E. Rauhala

Accelerator Laboratory, University of Helsinki, P.O. Box 43, FIN-00014 University of Helsinki, Finland

P. Uusimaa

Department of Physics, Tampere University of Technology, P.O. Box 692, FIN-33101 Tampere, Finland

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Diffusion of platinum in zinc selenide has been studied by the use of the ^4He and ^{12}C ion backscattering techniques. The samples were thin films grown by molecular beam epitaxy on GaAs (100) epitaxial layers followed by evaporation of platinum and annealing in the temperature range 500–800 °C. The diffusion coefficients were determined by the fitting of a concentration independent solution of the diffusion equation to the experimental depth profiles. The activation energy and the pre-exponential factor of the diffusion process were found to be 1.7 eV and $6.4 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively. © 1998 American Institute of Physics. [S0003-6951(98)00220-4]

Zinc selenide as a base for blue light emitting diodes and blue semiconductor lasers has gained increased attention in the last few years. In order to make these devices work it is of great importance to be able to construct a thermally stable ohmic contact to the semiconductor. These contacts are often heterostructures consisting of many different metals, for example Pt, Au, Ti and Ni,^{1–4} and to improve the contact properties they often have to be annealed at temperatures up to 350 °C for 45 min.⁵ It is thus of prime importance to know the thermal stability of such a metal/semiconductor heterostructure.

Previously some research has been done on the electrical properties of Pt/ZnSe heterostructures^{1,6} and interfacial reactions.⁷ Some of these studies report indiffusion of platinum and outdiffusion of zinc, but they do not, however, report any quantitative data of the diffusion of platinum in ZnSe. In this letter we report on the activation energy and pre-exponential factor for the diffusion of platinum in ZnSe.

Unintentionally doped *n*-type ZnSe was grown on an epitaxial *p*-GaAs buffer layer. The growth temperature and the beam pressure ratio (Se:Zn) of the layers were 290 °C and 2:1, respectively. The thickness of the ZnSe layer was 1.9 μm . At this thickness the layer structure was relaxed, due to lattice mismatch between GaAs and ZnSe. The lattice relaxation was confirmed by x-ray diffraction measurement for each sample. After growth the sample sets were immediately transferred to an *e*-beam vacuum evaporator chamber, where a 10 nm thick platinum layer was deposited onto one of the sample sets (labeled I) and a 100 nm thick platinum layer onto a second one (labeled II). The two thicknesses of platinum were deposited on the ZnSe in order to study the effect of the metal film thickness 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–48 h in the temperature range 550–800 °C. The annealing temperatures were measured with a calibrated chromel–alumel thermocouple in close contact with the samples. In order to protect the sample

surfaces, the samples were encapsulated by silicon wafers during annealing.

Previous studies of metal contacts on compound semiconductors have shown grain formation on the sample surfaces.^{2,8–11} We, therefore, studied the sample surfaces with scanning electron microscopy (SEM). This study showed grain formation on the surfaces of sample series II (platinum layer thickness 100 nm). By monitoring the characteristic x-ray emission while scanning the samples we could conclude that the grains consisted of zinc. This is in agreement with previous reports.⁷ In Fig. 1 we show an example of a SEM micrograph of sample series II. However, the surfaces of sample series I (platinum layer thickness 10 nm) were, as can be seen from Fig. 2, much smoother than the surfaces of sample series II. It is noteworthy that the samples in Figs. 1 and 2 were annealed at the same temperature.

Rutherford backscattering spectrometry (RBS) was used to determine the concentration profiles. Sample series I was measured with a 2.5 MeV ^4He beam obtained from a 2.5 MV

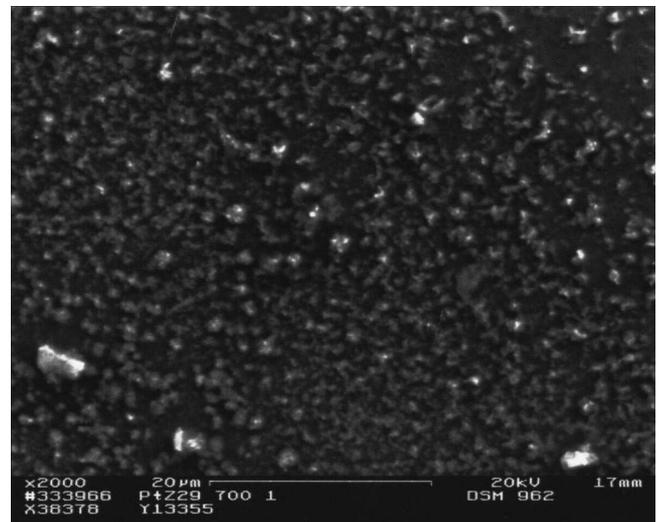


FIG. 1. Typical secondary electron SEM micrograph ($60 \mu\text{m} \times 45 \mu\text{m}$) of the surface of sample series II (platinum layer thickness 100 nm). The sample was annealed for 1 h at 700 °C.

^{a)}Author to whom correspondence should be addressed; Fax: +358 9 1918378; electronic mail: cjslotte@kruuna.helsinki.fi

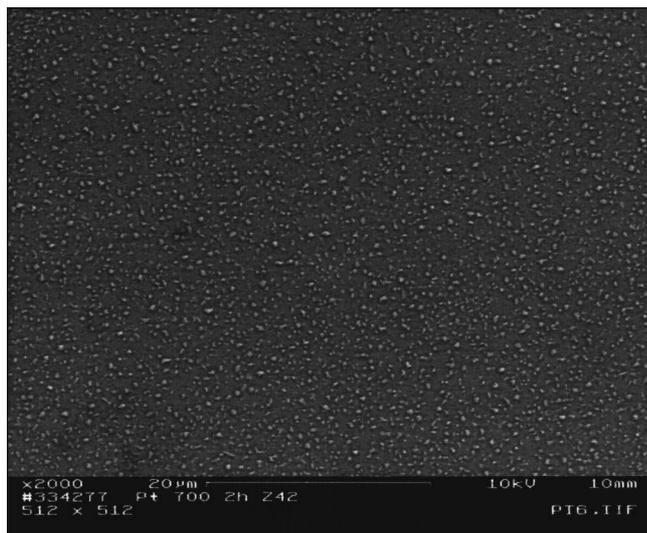


FIG. 2. Typical secondary electron SEM micrograph (60 μm×45 μm) of the surface of sample series I (platinum layer thickness 10 nm). The sample was annealed for 2 h at 700 °C.

Van de Graaff accelerator at the accelerator laboratory. The scattering angle was 170° and the angle of incidence 5°. Examples of different spectra are presented in Fig. 3. Concentration profiles for sample series II could not be obtained with 2.5 MeV ⁴He backscattering since the signal from the diffused platinum overlapped the signal from the ZnSe, which made it difficult to determine the depth profiles correctly. We therefore measured these samples with a 15 MeV ¹²C beam from the accelerator laboratory's 5 MV tandem accelerator EGP-10-II. The scattering angle in these measurements was 165° and the angle of incidence 7°. In these spectra the diffused platinum signal could clearly be distinguished from the ZnSe signal. The concentration profiles were extracted from the RBS spectra by use of the computer program GISA 3.99.¹²

The diffusion coefficients were determined by the use of a concentration independent diffusion model. The solution to the diffusion equation for an infinite diffusion source and an infinite medium,¹³

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

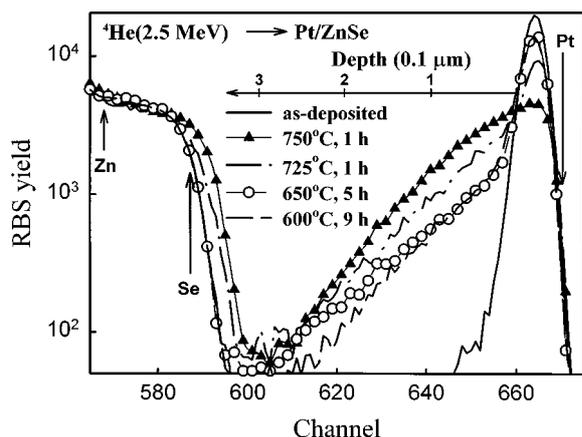


FIG. 3. Examples of 2.5 MeV ⁴He RBS spectra of sample series I (platinum layer thickness 10 nm), with an approximate depth scale. The scattering angle was 170° and the angle of incidence 5°.

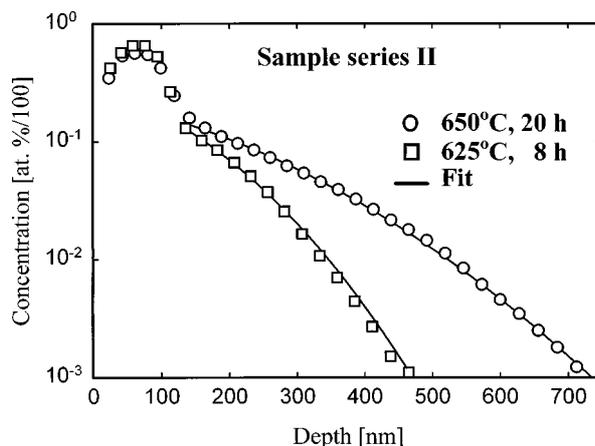


FIG. 4. Examples of least squares fits to depth profiles obtained by 15 MeV ¹²C ion backscattering. The samples (series II, platinum layer thickness 100 nm) were annealed at 650 °C for 20 h and 625 °C for 8 h.

was fitted, with the least squares method, to the depth profiles. Here *C* is the concentration of platinum, *D* is the diffusion coefficient, *x* is the depth, *t* the diffusion time, and *erfc*(*x*) the complementary error function. Examples of fits can be seen in Fig. 4.

The activation energy and pre-exponential factor for the diffusion of platinum in ZnSe were calculated from the Arrhenius plot log *D* vs 1/*T* (inverse annealing temperature) (see Fig. 5). These were found to be 1.7 eV and 6.4 × 10⁻⁶ cm²/s, respectively. The Arrhenius plot also shows that the results for the two sample series are in good agreement. Thus, neither the thickness of the platinum layer nor significant zinc grain formation on the surfaces of sample series II affect the diffusion results.

The results of Duxstad *et al.*⁷ show significant changes in the RBS spectra after only 10–30 min of annealing in the temperature interval 575–650 °C. These results cannot, however, be directly compared to this study, since etching in HF and backspattering with Ar⁺ ions was used prior to metal deposition. We have observed in a previous study that backspattering prior to metal deposition enhances diffusion.¹⁴ Duxstad *et al.* also report that backspattering of the ZnSe was needed to obtain a consistent reaction of platinum on ZnSe.

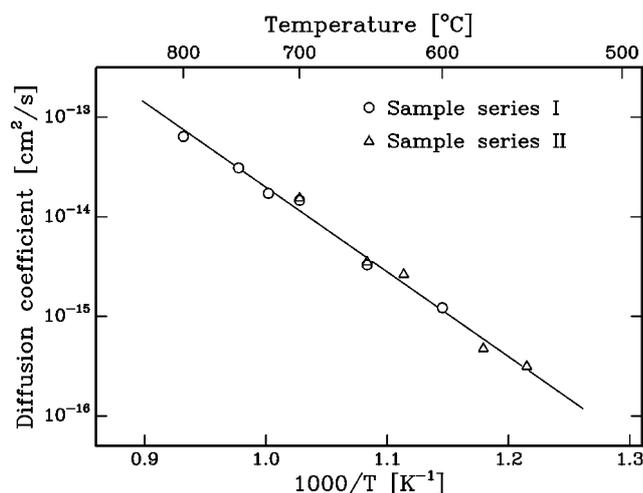


FIG. 5. Arrhenius plot of the diffusion coefficients for the two sample series.

By fitting the solution of the diffusion equation combined with a chemical reaction,¹³ we could conclude that the chemical reaction was negligible compared to the diffusion. Thus, in our study the reaction of platinum on ZnSe need not be taken into account.

We conclude this letter by noting that the diffusion of platinum in ZnSe is negligible in the process of preparing ohmic contacts. The annealing of Pt/ZnSe contacts in 400 °C for 45 min would only result in a diffusion length of approximately 1 nm.

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