Experimental Study of Ternary Pd-Zn-Se Phase Equilibria and Pd/ZnSe Bulk Diffusion

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The ternary system Pd-Zn-Se was investigated at 340 °C. A complete isothermal phase diagram is given, containing the formerly known ternary phase Pd_5ZnSe (τ_1) as well as a newly discovered ternary phase τ_2 of approximate composition $Pd_{62}Zn_{32}Se_6$. The reaction diffusion between Pd and ZnSe was investigated at 340 °C with bulk diffusion couples Pd/ZnSe, annealed from 6 to 192 h, and the diffusion path is described. For the investigation x-ray powder diffraction, scanning electron microscopy, and energy dispersive x-ray analysis was used. Implications for the application of Pd as metallic contact to semiconducting ZnSe are outlined.

1. Introduction

The realization of blue-light emission in solid-state optoelectronic devices is one major challenge in current research. Typical applications are full color displays, light-emitting diodes (LEDs), and laser devices for high-density optical storage. To obtain light in the desired wavelength region, semiconductors with a large bandgap (>2.5 eV) have to be used. ZnSe fulfills this requirement and is one of the materials undergoing significant research efforts at present [94Beh].

A major obstacle for the achievement of suitable devices are interface reactions between semiconductor and electrical contacts, which are usually made of single or multilayer metals. For the successful realization of metal contacts on ZnSe, a profound knowledge of the phase equilibria in the system concerned is indispensable.

For the binary systems involved, literature data are as follows: the Zn-Se system is generally accepted [90Mas]. The Pd-Zn system in [90Mas] is essentially from [51Kos] with an additional phase $PdZn_2$ from [78Ala]. The Pd-Se system was taken from [90Mas], based primarily on [79Ols] and [87Tak].

One ternary compound τ_1 (Pd_5ZnSe) was reported [70Elb] and was observed also in an investigation about solid-state reactions in Pd/ZnSe thin-film contacts [95Dux]. Phase equilibria in the Pd-Zn-Se system are not reported.

The purpose of this study is to establish ternary phase equilibria in the Pd-Zn-Se system and to investigate solid-state reaction diffusion in an annealing process of Pd on ZnSe. In a second paper, the resulting electrical properties are discussed [97Sch].

The authors investigated in detail the ternary section of Pd-Zn-Se at 340 °C by optical and x-ray techniques. To define useful sample compositions for the experimental investigation, they started with approximate calculations of the ternary phase equilibria. To obtain knowledge of the interface kinetics between ZnSe and the contact metal Pd they prepared bulk diffusion couples. Investigation was then performed using scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX).

2. Approximate Calculations of Ternary Phase Equilibria

In order to get a first idea of the possible phase equilibria in the Pd-Zn-Se system at 340 °C, an approximate calculation was performed using the software TerQuat (freeware) [92Kli]. These calculations are useful to define sample compositions for the experimental investigation. The program assumes no mutual solubilities, and all phases are taken as stoichiometric. The Gibbs energy of formation, ΔG, for ZnSe was taken from [89Bar]. Some thermodynamic data for ΔG in the Pd-Se system are from [89Bar], some are estimated because not all compounds are listed. No data were found for the Pd-Zn system, therefore $\Delta G \approx \Delta H$ of compounds have been calculated using Miedema's model [83Nie]. The Gibbs energy of formation for τ_1 is estimated to be in the range of 30 ± 2.5 kJ/mol-atoms in order to make τ_1 stable at 340 °C. Figure 1 shows the calculated ternary section for 340 °C, dashed tie lines represent less probable, alternative equilibria that are obtained if an error of ±8 kJ/mol-atoms is allowed for the ΔG values.

One can see that ZnSe is not in equilibrium with Pd; τ_1 is located right between the two phases. Pd is in equilibrium with τ_1, but there is no tie line between τ_1 and ZnSe. The most questionable equilibrium is Pd_2Zn-ZnSe, which is intersected by several dashed lines. Another possibility would be a tie line τ_1-ZnSe. With these calculations as a first indication for probable phase equilibria, meaningful experimental investigations could be performed and are presented in the following.

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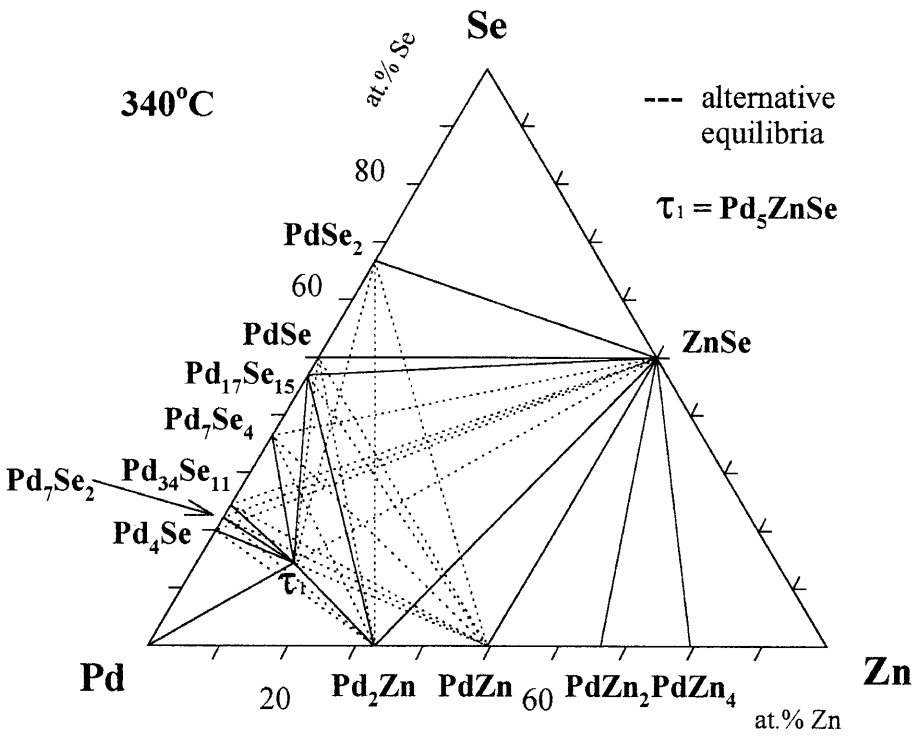

Fig. 1 Pd-Zn-Se phase equilibria at 340 °C, approximately calculated with TerQuat [92Kli]. Dotted lines represent less probable equilibria. The program does not consider mutual solubilities, and the compounds are taken as stoichiometric. The contact metal Pd is not in equilibrium with ZnSe but with τ_1.

3. Experimental

3.1 Investigation of Ternary Phase Equilibria

3.1.1 Sample Preparation

Sample synthesis was performed from pure elements, starting materials were generally used as powder with a purity of 99.9%. If possible, pure Se was substituted by ZnSe because of the high toxicity and vapor pressure of pure Se. The powder mixture was cold pressed into pellets using a pressure of 430 MPa. The pellets were put in silica ampoules, evacuated, and sealed. Annealing was performed at 340 °C, done in two steps. Most of the samples showed a strong initial reaction after only a few minutes. These samples were then powdered in a ball mill if necessary, pelleted, and sealed again as described above. The second anneal took 3 to 56 days to ensure complete reaction, which was monitored by XRD. If the signals were still changing, the samples were annealed further. After annealing the samples were quenched in water and powdered for detailed x-ray investigation.

3.1.2 X-Ray Diffraction

The powdered samples were investigated in a Siemens D5000 diffractometer (Bruker AXS, Karlsruhe, Germany) with Co-Kα radiation and Fe filter. The indexing of the spectra was performed using PDF data [ICDD]. If no such files were available, the spectra were calculated using structure data from [91Vil] and the computer program PowderCell (freeware) [94Kra].

3.2 Investigation of Bulk Diffusion Couples

3.2.1 Sample Preparation

For bulk diffusion couples, small pieces of large-grain, polycrystalline ZnSe ($\sim 3 \times 3 \times 4$ mm^3) with parallel flat faces were used. These crystals were rinsed in acetone and water. Pieces of Pd foil of 250 μm thickness were mechanically pressed on the flat faces. These sandwichlike samples were annealed under uniaxial pressure of approximately 3 MPa at 340 °C for various times up to a maximum of 192 h under vacuum (10^{-2} mbar). After annealing, the samples were embedded in resin, cross sectioned, and metallographically polished down to 0.1 μm oxide polishing suspension (OPS) finish for further analysis.

3.2.2 Scanning Electron Microscope and Energy-Dispersive X-Ray Investigation

SEM with EDX microanalysis was used to determine various phases and compositions in the diffusion couples. The samples were used directly after polishing without further coating. The operating voltage used was 30 keV. A standard ZAF (Z: order number, A: absorption, F: fluorescence) routine converted intensities into compositions [94Fio].

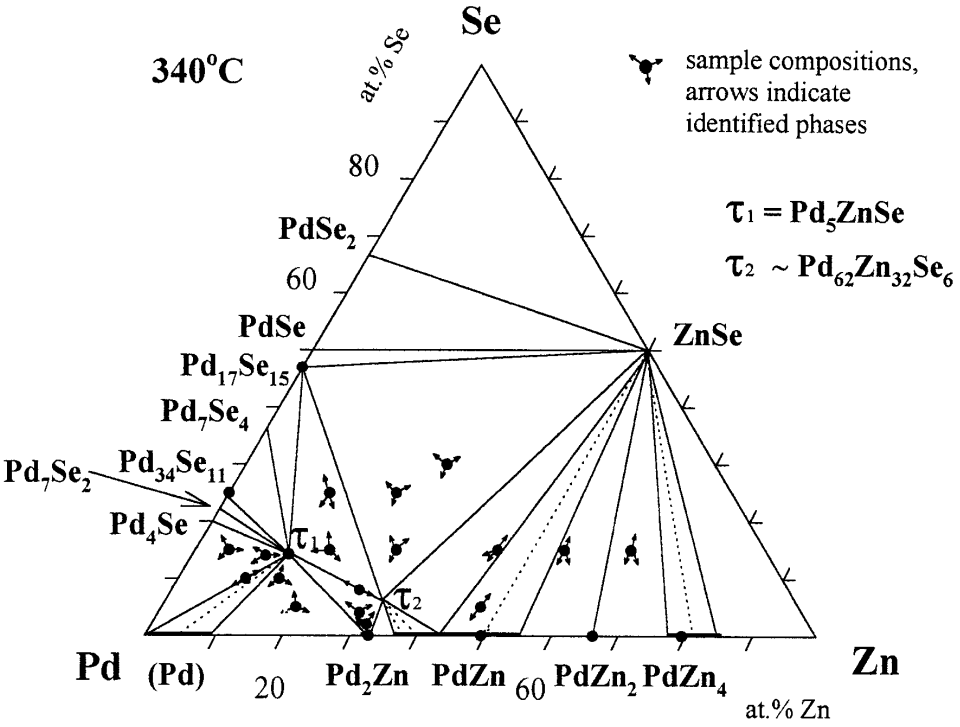

Fig. 2 Experimentally determined Pd-Zn-Se equilibria at 340 °C. The binary systems were taken from [90Mas]. Solid dots represent binary and ternary sample compositions used for the investigations. Arrows are pointing to the phases detected in the sample. Extended two-phase fields are indicated by one dotted tie line. A second ternary phase ($\tau_2 \sim Pd_{62}Zn_{32}Se_6$) could be identified.

4. Results

4.1 Ternary Phase Diagram

The annealing was done in two steps as described above. Already after minutes of annealing a spontaneous reaction occurred and the phase τ_1, as identified with XRD, was found. This was mainly observed for samples clearly inside the area confined by Pd, PdZn, ZnSe, and $Pd_{17}Se_{15}$. However, the samples were not necessarily completely reacted because after additional annealing the content of phases changed, some even disappeared. After 56 days, at the most, the reactions were considered complete because no change in phase composition was observed and the number of phases detected complied with the phase rule, as seen in Fig. 2.

Figure 2 shows the experimentally determined isothermal section of the Pd-Zn-Se phase diagram at 340 °C. The binary systems were taken from [90Mas]. All occurring solid phases are compiled in Table 1. Only samples with Se content lower than 50 at.% were prepared because the equilibria above this line were unambiguous.

Six binary and 18 ternary samples were investigated. The sample compositions are indicated by the black dots in the figure, arrows indicate the phases found. Important binary phases have been confirmed in single-phase samples, indicated as solid dots without arrows in Fig. 2. Each binary Pd-Zn phase was prepared as well as $Pd_{17}Se_{15}$ and $Pd_{34}Se_{11}$. One ternary

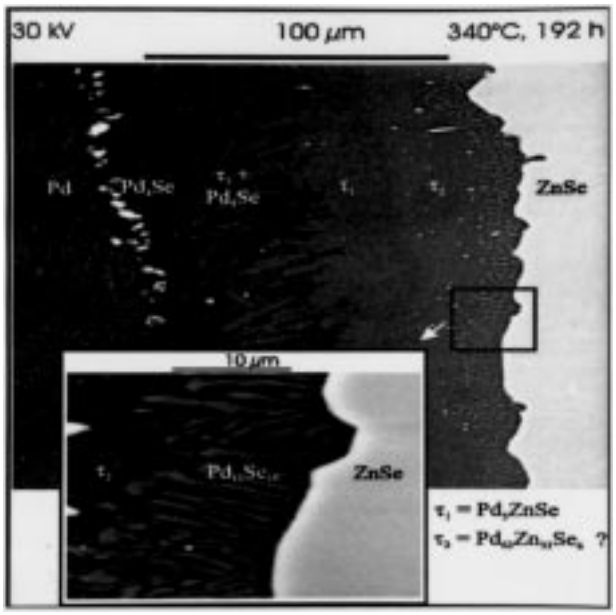

Fig. 3 Cross section of a Pd/ZnSe bulk diffusion couple after annealing for 192 h at 340 °C (backscattered electron image). The sequence of phases in the reaction zone is $Pd/Pd_4Se/Pd_4Se + \tau_1/\tau_1/\tau_2/\tau_2 + Pd_{17}Se_{15}/ZnSe$.

Table 1 Solid Phases Observed at 340 °C in the System Pd-Zn-Se, Structural Data and Temperature Stabilities

Solid phases	Composition, at.%	Pearson symbol	Space group	Lattice parameters, nm a_0	b_0	c_0	Comment	Temperature stability, °C	Reference
(Zn)	100 Zn	*hP*2	$P6_3/mmc$	0.2665	…	0.4947	…	<419.6	[90Mas, 91Vil]
(Se)	100 Se	*hP*3	$P3_121$	0.4366	…	0.4954	…	<221	[90Mas, 91Vil]
ZnSe	50 Se	*cF*8	*F*43*m*	0.5663	…	…	…	<1526	[90Mas, 91Vil]
(Pd)	0 Se 0, ~/0 Zn	*cF*2	*Fm*3*m*	0.389	…	…	…	1555	[90Mas, 91Vil]
Pd_4Se	20 Se	*tP*10	$P42_1c$	0.5232	…	0.565	…	527	[90Mas, 91Vil]
Pd_7Se_2	22.2 Se	*m**18	…	0.9462	0.5354	0.55	β = 86.5°	544	[90Mas, 91Vil]
$Pd_{34}Se_{11}$	24.4 Se	*mP*90	$P2_1/c$	1.203	0.5504	2.278	β = 112°	430	[90Mas, 91Vil]
Pd_7Se_4	36.4 Se	*oP*22	$P2_12_12$	1.0162	0.6863	0.538	…	415	[90Mas, 91Vil]
$Pd_{17}Se_{15}$	46.9 Se	*cP*64	*Pm*3*m*	1.0606	…	…	…	680	[90Mas, 91Vil]
PdSe	50 Se	*tP*16	$P4_2/m$	0.673	…	0.691	…	620	[90Mas, 91Vil]
$PdSe_2$	66.7 Se	*oP*12	*Pbca*	0.572	0.58	0.767	…	760	[90Mas, 91Vil]
Pd_2Zn	33.3 Zn	*cP*12	*Pnma*	0.535	0.414	0.765	…	~700	[90Mas, 91Vil]
PdZn	50 Zn	*tP*4	*P*4/*mm*	0.410	…	0.335	…	~1200	[90Mas, 91Vil]
$PdZn_2$	66.7 Zn	*oC*48	*Cmmm*	0.753	0.736	1.231	…	~530	[90Mas, 91Vil]
$PdZn_4$	81.6 Zn	…	?	0.911	…	…	…	880	[58Han, ICCD]
t_1 (Pd_5ZnSe)	71.42Pd, 14.29 Zn, 14.29 Se	…	…	0.395	0.691	0.175	…	…	[70Elb]
t_2 (~$Pd_{62}Zn_{32}Se_6$)	62 Pd, 32 Zn, 6 Se	…	…	…	…	…	…	…	This work

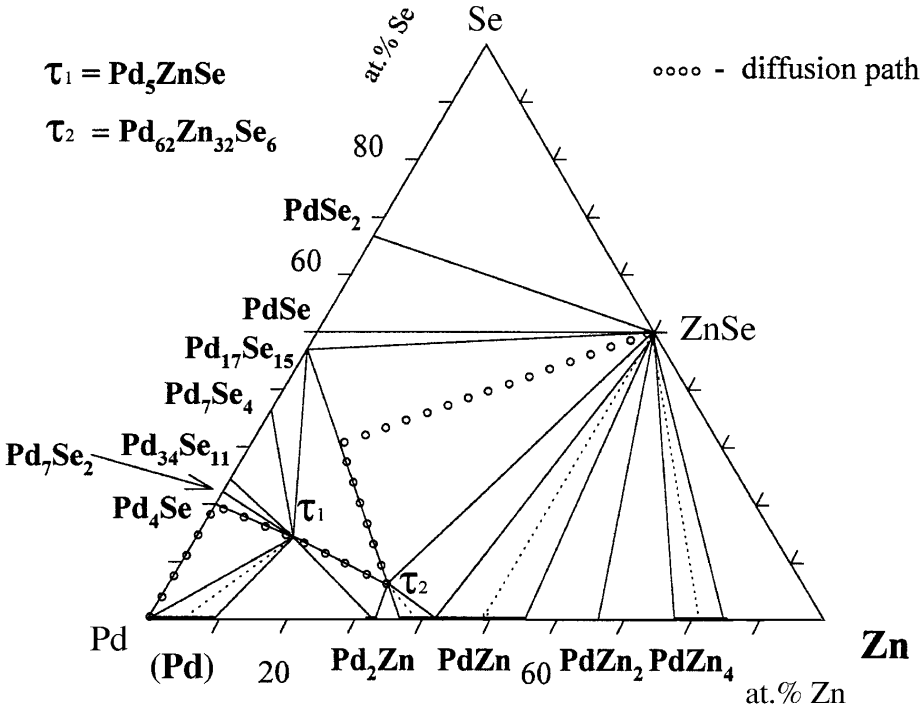

Fig. 4 Isothermal section of the phase diagram Pd-Zn-Se with the diffusion path in the diffusion couple Pd/ZnSe indicated by the open circles.

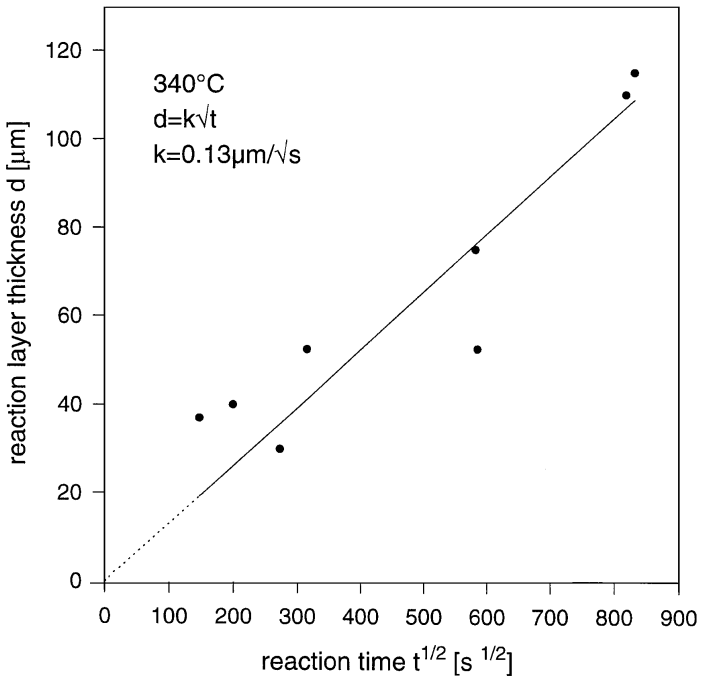

Fig. 5 Thickness of the total reaction layer plotted against the square root of the annealing time. The growth of the layer thickness follows a parabolic law.

compound τ_1 (Pd_5ZnSe), which was already known from literature [70Elb] was prepared stoichiometrically. It was also identified in the multiphase samples surrounding τ_1.

A second ternary compound τ_2 was found that was not previously reported in literature. Samples prepared in the region $Pd_{17}Se_{15}$-τ_1-Pd_2Zn-ZnSe revealed a phase similar to Pd_2Zn but with different x-ray data. The authors interpret this as the development of a new phase in the region near Pd_2Zn. This phase is definitely not just a ternary solubility of Se in Pd_2Zn because some samples contained three distinctly different phases, namely τ_1, Pd_2Zn, and τ_2. The approximate composition of τ_2 is $Pd_{62}Zn_{32}Se_6$.

The phase τ_1 is in equilibrium with several Pd-rich phases. The key equilibrium in Fig. 2 is the three-phase field ZnSe-τ_2-$Pd_{17}Se_{15}$.

4.2 Bulk Diffusion Couples

Figure 3 shows the backscattered electron image of a cross section of a bulk diffusion couple Pd/ZnSe annealed at 340 °C for 192 h. The dark edge at the left-hand side of the picture shows part of the remaining Pd foil, the bright side represents the residual bulk ZnSe.

Between these starting phases, a wide reaction zone can be seen with several compounds developed in the solid state even at this low temperature. The identification of the phases was performed with EDX in spot and line scan mode. Reading from the left, the following sequence of phases is found: in contact with Pd is Pd_4Se. The white dots in the Pd_4Se are a porosity probably originating from the metallographic preparation procedure because the density of these holes increased with polishing time. The holes are not a typical feature of the reaction zone, but were found in this sample only. A two-phase region exists between Pd_4Se and Pd_5ZnSe (τ_1) and consists of these two compounds. Next is a band of pure τ_1 followed by pure τ_2. Between ZnSe and τ_2 a cellular transition region can be seen (see also enlarged region). It was identified as $Pd_{17}Se_{15}$ + τ_2. This cellular region next to ZnSe is observed after all, even the shortest, annealing times. The complete sequence of reaction products in a Pd/ZnSe diffusion couple is visualized as the diffusion path, indicated by the open circles, in Fig. 4. It is Pd/Pd_4Se/Pd_4Se + τ_1/τ_1/τ_2/τ_2 + $Pd_{17}Se_{15}$/ZnSe.

In Fig. 5, the total reaction layer thickness is plotted against the square root of the annealing time. If a linear dependence was observed, this would indicate an overall diffusion-controlled growth of the layer. The linear fit in Fig. 5 is not very good but still not unjustifiable. If fitted to the equation $d = k\sqrt{t}$, a reaction constant of k = 0.13 µm/$\sqrt{s}$ is obtained ($k^2 = 1.7 \times 10^{-10}$ cm^2/s).

At the edges of the sample where the Pd foil had no contact to the bulk ZnSe, it can be seen that the direction of phase growth is from the ZnSe toward Pd foil.

5. Discussion

The ternary section Pd-Zn-Se at 340 °C is on the one hand obviously dominated in the Pd-rich region by the ternary com-

pound τ_1(Pd_5ZnSe) and the resulting three-phase fields. On the other hand stable tie lines leading from ZnSe to the Pd-Zn compounds determine the phase relationships in the Zn-rich region. These results from the key equilibrium ZnSe + τ_2 + $Pd_{17}Se_{15}$. The calculations of the ternary section with TerQuat in principle agree with the determined phase relations, keeping in mind that TerQuat does not support any solubilities. A difference results from not considering τ_2 in the initial calculations. However, the dominant role of Pd_5ZnSe (τ_1) is confirmed in both the calculations and the experimental investigations. Another indication of the high thermodynamic stability of τ_1 is the observation that the (Pd)-vertex of the three-phase equilibrium (Pd) + τ_1 + Pd_4Se is shifted only very slightly to the Zn-direction. The occurrence of an analogous ternary phase τ_1 with the observed sample composition is already known for the systems Pd/GaAs and Pd/InP [70Elb] but also for Pd/ZnSe [95Dux]. The existence of the new ternary compound τ_2 was concluded from x-ray data that are different from those of Pd_2Zn. It should be noted that τ_2 forms much slower than τ_1 in (Pd + ZnSe) powder samples. No further attempt has been made to examine structure or composition of the new phase τ_2 in detail.

The authors' investigations of bulk diffusion couples show the reaction diffusion process if both the ZnSe crystal and the Pd represent an unlimited reservoir. From the bulk diffusion couple the quasi-stationary diffusion path of Pd/ZnSe can be deduced. It is:

$Pd/Pd_4Se/Pd_4Se + \tau_1/\tau_1/\tau_2/\tau_2 + Pd_{17}Se_{15}/ZnSe$

This is in complete agreement with the experimentally determined isothermal section of the phase diagram, which implies that local equilibria prevail at the interfaces, as detailed in Fig. 4. The phase sequence observed did not depend on the annealing time. As opposed to the powder samples no primary reaction with τ_1 as a dominant (transient) was found; however, the shortest annealing time for the diffusion couples was 6 h.

At the end of the diffusion process, the existence of three phases, τ_2, $Pd_{17}Se_{15}$, and ZnSe could be expected if the Pd is completely consumed. The fact that the complete Pd layer is converted into reaction products point to some promising conclusions for the electrical contact properties. No further reactions should be expected during device operation or storage; this could lead to stable characteristics. Especially at low temperatures (starting with 200 °C), a solid-state reaction may be beneficial to avoid a degradation of the electrical properties of the ZnSe film.

6. Conclusions

- The phase equilibria in the 340 °C isothermal section of the ternary Pd-Zn-Se system were determined.
- A new ternary phase τ_2 of approximate composition $Pd_{62}Zn_{32}Se_6$ was found.
- The diffusion path in a bulk diffusion couple Pd/ZnSe is: $Pd/Pd_4Se/Pd_4Se + \tau_1/\tau_1/\tau_2/\tau_2 + Pd_{17}Se_{15}/ZnSe$
- The reaction layer most probably grows according to a parabolic law.

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