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Neutron transmutation doping as an experimental probe for $\mathrm{As}_{\mathrm{Se}}$ in ZnSe

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An experimental investigation of the effects of isolated arsenic atoms at substitutional selenium sites in ZnSe is presented. Two methods employing neutron transmutation doping and utilizing the long half-life of ^{75}Se to introduce $\mathrm{As}_{\mathrm{Se}}$ dopants in ZnSe are described. In the first method, bulk ZnSe is neutron irradiated and then annealed before significant decay of ^{75}Se occurs. In the second method, a post-neutron-irradiation homoepitaxial crystal-growth technique is used where the ^{75}As decay product is incorporated in an epitaxial layer of ZnSe *after* the epitaxial layer is grown. Since the nuclear recoils associated with the decay of ^{75}Se to ^{75}As are too small to displace the arsenic atoms from their selenium sites, arsenic doping at selenium sites is ensured. [S0163-1829(96)06623-4]

I. INTRODUCTION

Zinc selenide is one candidate for a blue light emitter. As with all wide-band-gap II-VI compound semiconductors, ambipolar doping has proven difficult in ZnSe. In ZnSe, effective p-type doping is both difficult to obtain and poorly understood. Recent success in obtaining p-type ZnSe by employing nitrogen as a dopant raises hopes that a reliable blue light emitter based on ZnSe is possible.[1,2] This success with nitrogen suggests further investigation of other group-V elements in ZnSe. Bhargava has emphasized the importance further investigation of other group-V dopants may hold for understanding dopant behavior in ZnSe.[3]

Early work in arsenic-doped ZnSe suggested arsenic forms a deep acceptor and is not suitable for achieving low p-type conductivity.[4,5] These experimental observations are consistent with the theoretical work of Chadi and co-workers predicting a deep distorted center.[6–8] Later experimental work showed that arsenic doping results in a shallow level in ZnSe with both shallow and deep levels appearing at higher dopant concentrations.[9] In a recent study, arsenic was shown to form a shallow hydrogenic center in ZnSe.[10] Magnetospectroscopy was employed to determine the doping center's symmetry which was consistent with arsenic at a selenium site. In another recent study, site-selective metal organic vapor phase epitaxy (MOVPE) was employed to introduce arsenic at selenium sites in ZnSe.[11] Again, a shallow level was observed at low doping concentrations with a deeper level appearing only at higher doping concentrations. Recent theoretical work by Kwak, King-Smith, and Vanderbilt on phosphorous doping in ZnSe gives no support for the deep DX-type center predicted in Chadi's work.[12] An investigation of phosphorous doping in ZnSe is germane here, since the behavior of phosphorous in ZnSe is similar to that of arsenic. In this study it is predicted that a deep center may be associated with an interstitial phosphorous dopant. The symmetry of this center is consistent with the earlier experimental work investigating the deep center associated with arsenic.[4,5] This theoretical investigation indicates that phosphorous at a zinc site may be an effective compensation mechanism in ZnSe.

The above discussion illustrates that understanding arsenic doping in ZnSe is important and that no clear understanding presently exists. One consistent experimental observation is that arsenic introduces only shallow centers at low concentrations and introduces both shallow and deep centers at higher concentrations. In addition to the models proposed by Chadi and Kwak, King-Smith, and Vanderbilt, the solubility limitations suggested by Neumark,[13] or a dopant-lattice interaction during growth resulting in self-compensation effects, as suggested by Mandel[14] and Marfaing,[15] are consistent with this observation as is recent work by Garcia and Northrup[16] on dopant-lattice interactions. The observation that a deep level consistently appears at high dopant concentrations suggests some type of interaction may be present during crystal growth. That is, the fashion in which the arsenic dopant is incorporated in ZnSe lattice may be a function of the concentration of arsenic atoms present at the time of crystal growth. The interactions present at high dopant concentrations may include dopant-lattice interactions and interactions between arsenic dopants. If this coupling between crystal growth and doping processes is removed, doping and compensation processes in ZnSe could be experimentally probed in additional ways.

Neutron transmutation doping (NTD) provides an opportunity to study arsenic doping in ZnSe. In this study, neutron transmutation is employed to introduce $\mathrm{As}_{\mathrm{Se}}$, which is thought to be the dopant center responsible for the observed shallow level in arsenic-doped ZnSe.[10] Characterization techniques include low-temperature photoluminescence (PL) and x-ray diffraction.

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II. EXPERIMENT

Two different experimental techniques for transmutation doping are reported here. In the first technique, ⟨100⟩ ZnSe crystals are neutron irradiated and then annealed. In the second technique, epitaxial layers of ZnSe are grown from zinc and neutron-irradiated selenium on ⟨111⟩ ZnSe substrates.

A. Irradiation of ZnSe crystals

Seeded physical vapor transport (SPVT)-grown ZnSe crystals measuring $1 \times 1 \times 0.25$ mm^3 obtained from Eagle Picher Laboratories in Miami, Oklahoma, were exposed to thermal neutrons at the Missouri University Research Reactor facility in Columbia, Missouri. The exposure results in 10^{17}-cm^{-3} ^{74}Se nuclei capturing thermal neutrons to form ^{75}Se nuclei which decay by electron capture of ^{75}As. The half-life of the decay is 118.5 days. The long half-life of ^{75}Se is crucial in this technique because it allows sufficient time for annealing before nuclear decay.

During neutron irradiation, the ZnSe crystals suffer lattice damage due to both fast neutron collisions and nuclear recoils associated with the emission of prompt γ rays during radiative capture of thermal neutrons. To remove this lattice damage, the irradiated crystals were annealed in sealed quartz vials for 1 and 3 h at temperatures from 600–900 °C in an atmosphere of high-purity argon. Temperatures in this range were previously employed for ion implantation studies in ZnSe.[17] Several grams of ZnSe were placed in the quartz vials to surround the small irradiated crystals during the anneals.

B. Homoepitaxial growth by physical vapor transport of the elements

In order to develop a technique where crystal growth and doping are decoupled, with no need for high-temperature annealing, a closed-tube homoepitaxial growth technique was developed in this work. While other epitaxial growth techniques with elemental zinc and selenium as source materials would serve equally well, this closed-tube technique does not result in expensive epitaxial deposition equipment being contaminated, and significantly reduces the experimental hazard present when using radioactive source material. Epitaxial layers of ZnSe are grown on SPVT ZnSe substrates. The resulting epitaxial layers are typically tens of micrometers thick, as determined by their post-growth activity. The source material is high-purity zinc and high-purity selenium previously irradiated with thermal neutrons, so that 10^{17} cm^{-3} ^{74}Se nuclei have captured thermal neutrons to form ^{75}Se, which then decays to ^{75}As by electron capture. Here again, the long half-life of ^{75}Se is crucial, since it allows the epitaxial layer to be grown before significant transmutation has occurred. Experimental details of the homoepitaxial growth technique will be presented elsewhere.[18]

C. Photoluminescence and x-ray-diffraction characterization

The PL spectra for ZnSe samples annealed at 600 °C for 3 h are shown in Fig. 1. Figure 1(a) shows the PL spectrum for unirradiated, annealed ZnSe. This spectrum is used for comparison to allow the effects of irradiation to be isolated from the effects of just annealing. Figure 1(b) shows the PL spectrum of irradiated ZnSe one month after irradiation. Figure 1(c) shows the PL spectrum for the same irradiated sample four months after irradiation. A free-exciton (FE) peak at 2.802 eV is present in the unirradiated sample. The donor bound exiton (DBE) peak at 2.7973 eV labeled I_2 is due to a shallow donor. The dominant I_1^d exitonic emission at 2.7830 eV is typical of bulk ZnSe and is thought to result from zinc vacancies (V_{Zn}) (Refs. 19 and 20) and copper substituting on a zinc site (Cu $_{\mathrm{Zn}}$).[21–23] It has several longitudinal-optical-phonon replicas spaced 0.031 eV apart. This I_1^d peak and its phonon replicas in the SPVT-grown ZnSe, along with the DBE peak at 2.7973 eV, dominate the PL spectra above ~2.6 eV.

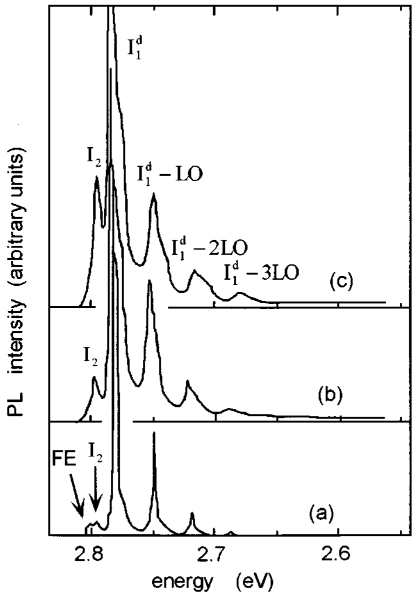

FIG. 1. PL spectra of bulk ZnSe. (a) Unirradiated ZnSe. (b) Irradiated ZnSe one month after irradiation. (c) Irradiated ZnSe four months after irradiation.

As seen in Fig. 1(b), the primary effect of the irradiation is to remove the FE peak, enhance the DBE peak at 2.7973 eV, and to broaden all the emission peaks. The increase in DBE intensity may be due to bromine at selenium sites and gallium at zinc sites which are undesirable effects of irradiating as-grown ZnSe. The absence of the FE peak and the broadening of the emission peaks indicates a higher level of lattice damage in the irradiated sample when compared to the unirradiated sample. This implies the annealing performed in this study does not fully remove all radiation damage.

The PL spectrum at four months after irradiation displays an enhanced DBE peak when compared to the spectrum one month after irradiation. Also, the location of this peak has moved from 2.7973 to 2.7960 eV. It is difficult to speculate on the cause of these changes since the region between the DBE and I_1^d has a high level of background emission. It may be noted, however, that a bound exiton at 2.7960 eV has been attributed to arsenic doping in ZnSe grown by MOVPE.[24]

Double-crystal x-ray diffraction and low-temperature PL were also employed to characterize structural and luminescent properties of the homoepitaxial layers grown in the second method. The full width at half maximum (FWHM) of

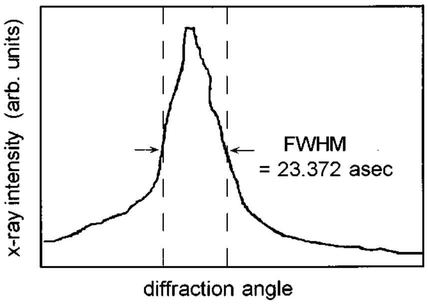

FIG. 2. Double-crystal x-ray-diffraction rocking curve of the ZnSe epitaxial layer.

the x-ray-diffraction rocking curve is less than 25 arc sec, which indicates a high degree of crystalline perfection as indicated in Fig. 2. This figure of 25 arc sec compares well the FWHM of near 10 arc sec for x-ray-diffraction peaks of SPVT-grown bulk ZnSe.[25] The layer's PL spectrum, taken one month after irradiation, is shown in Fig. 3. This PL spectrum displays no dominant I_1^d emission and low level of deep emissions. This strong evidence that isolated $\mathrm{As}_{\mathrm{Se}}$ centers at concentrations between 2×10^{16} and 3×10^{16} cm^{-3} do not result in the deep-level emissions that have been reported for the arsenic dopant in the past. In addition, this PL spectrum shows the homoepitaxial layer of ZnSe displays a sufficiently low level of background emissions to allow the effects of arsenic doping to be observed with PL.

The exiton peak shown in Fig. 3 is located at 2.7930 eV, which is closer in energy to an acceptor bound exiton (ABE) than the DBE at 2.7973 eV present in SPVT-grown ZnSe. Since the location of this peak is near the location of ABE peaks, and since arsenic is the only intentionally introduced p-type dopant in the epitaxially grown layer, one can speculate that the 2.7930-eV emission may be due to the arsenic dopant. Further work is necessary to assign the center responsible for this emission. The energy associated with the ABE attributed to the shallow arsenic center in other investigations is 2.7906 eV.[9,10]

III. DISCUSSION

The epitaxial technique has significant advantages as a probe for arsenic doping when compared to irradiating as-grown crystals of ZnSe. First, the lattice damage, caused by fast neutron collisions and nuclear recoils due to γ-ray emissions during the radiative capture of thermal neutrons, is eliminated since crystal growth occurs after irradiation. Since a significant number of radiative capture events for $^{74}\mathrm{Se}$,

$$^{74}\mathrm{Se}(n,\gamma)\,^{75}\mathrm{Se}, \tag{1}$$

results in γ rays of several MeV,[26] the recoil energy

$$E_R=\frac{E_\gamma^2}{2m_0c^2}\cong\frac{E_\gamma^2}{1.4\times10^5\ \mathrm{MeV}}, \tag{2}$$

where E_R is the recoil energy, E_γ is the γ-ray energy, m_0 is the nuclei mass, and c is the speed of light, is often sufficient to displace the dopant atom from its substitutional lattice position. Thus, in irradiating as-grown ZnSe crystals with thermal neutrons, many of the very atoms which would later form dopants are displaced. This displacement damage and that due to fast neutron lattice collisions must be removed by annealing to enable subsequent effects due to the nuclear decay to be observed without interference from unwanted defect structures. This experimental difficulty is avoided in the epitaxial technique, since epitaxial layer growth occurs after neutron irradiation. An additional advantage of the epitaxial technique is the PL spectrum of the epitaxial layer of ZnSe, shown in Fig. 3, displays no dominant I_1^d emission as is typically present in as-grown bulk ZnSe. It is desirable that the intensity of I_1^d be reduced, since the I_1^d emission and its phonon replicas can dominate the PL spectrum of ZnSe above ~2.6 eV. Without the I_1^d emission, the effects of ar-

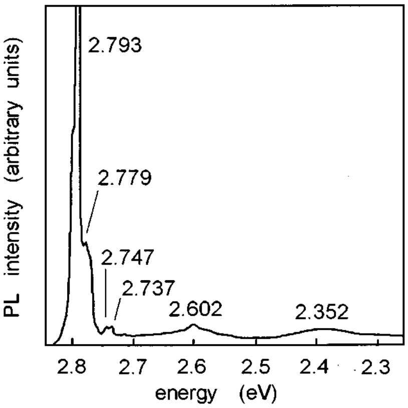

FIG. 3. PL spectrum of the ZnSe epitaxial layer grown from zinc and irradiated selenium.

TABLE I. Daughter nuclei from the neutron irradiation of zinc and selenium.

Selenium isotope	% abundance	Cross section (barns)	Daughter nuclei (normalized %)/half-life
$^{74}\mathrm{Se}$	0.87	46	$^{75}\mathrm{As}$ (3.5%)/118.5 days
$^{76}\mathrm{Se}$	9.0	22 + 63	$^{77}\mathrm{Se}$ (66%)
$^{77}\mathrm{Se}$	7.6	42	$^{78}\mathrm{Se}$ (28%)
$^{78}\mathrm{Se}$	23.5	0.38	$^{79}\mathrm{Se}$ (<0.01%) / not actually stable . . . half life ~ 60 000 years
$^{80}\mathrm{Se}$	49.8	0.07 + 0.39	$^{81}\mathrm{Br}$ (2%)/~1 h
$^{82}\mathrm{Se}$	9.2	0.039 + 0.006	$^{83}\mathrm{Kr}$ (<0.04%)/~3 h

TABLE II. Neutrino and γ-ray transition energies with the resultant nuclear recoil energies in the decay of ^{75}Se.

Transition energies (MeV)	Intensity (10^{-2}/decay)	Nuclear recoil (eV)	Transition energies (MeV)	Intensity (10^{-2}/decay)	Nuclear recoil (eV)
0.865	<5	5.36	0.280	21	0.56
0.666	<0.5	3.18	0.265	63	0.50
0.600	3	2.58	0.199	0.6	0.28
0.585	3	2.45	0.136	61	0.13
0.464	94	1.54	0.121	18	0.10
0.401	12	1.15	0.097	3.6	0.07
0.304	3.5	0.66	0.066	0.05	0.03

senic doping can be observed more easily. The third advantage is that elemental sources are employed in the epitaxial technique, allowing the effects of irradiating selenium to be separated from the effects due to zinc irradiation. This is not possible when irradiating as-grown ZnSe. In the epitaxial technique, the zinc source need not be irradiated when arsenic doping is being investigated. When irradiating as-grown ZnSe to investigate arsenic doping in ZnSe, both arsenic and bromine from the irradiation of selenium, and copper and gallium from the irradiation of zinc, are present. These additional factors complicate the interpretation of experimental observations. The final advantage of the epitaxial technique used here is that, since it uses only about 20 mg of each element, isotopically enhanced elements can be employed in future work at a much lower cost when compared to SPVT-grown ZnSe, since much smaller quantities of source materials are required.

The selenium isotope which decays to arsenic upon the radiative capture of thermal neutrons [Eq. (1)] is ^{74}Se, which decays by electron capture to ^{75}As,

$$^{75}\mathrm{Se}+e^{-}\rightarrow {}^{75}\mathrm{As}+\nu, \tag{3}$$

where ν is a neutrino. In naturally occurring selenium, ^{74}Se has an abundance of 0.87%. Table I (Refs. 27 and 28) shows that 3.5% of neutron captures in naturally occurring selenium produce arsenic, while 2% result in bromine, which acts as a donor on the selenium sublattice. Isotopically enriched selenium having a lower ^{80}Se content than naturally occurring selenium would improve the epitaxial technique's sensitivity as a probe for arsenic doping in ZnSe. This refinement remains for future work. Gamma rays and neutrinos are emitted during the decay of ^{75}Se to ^{75}Se. The energy of these γ rays and neutrinos is detailed in Table II.[28] The associated recoil energies are much lower than the displacement threshold energies reported for other materials.[29] This fact provides assurance that the dopant centers introduced into ZnSe epitaxial layers, formed from zinc and irradiated isotopically enhanced selenium, will be arsenic in isolated selenium sites.

IV. CONCLUSIONS

Recent experimental work on the arsenic dopant in ZnSe shows a shallow level is present at low doping concentrations, with both shallow and deep levels being present at higher doping concentrations. This observation suggests that some type of lattice or dopant interaction during crystal growth may be involved. An experimental technique which removes these interactions should be of interest. The experimental technique presented here allows isolated $\mathrm{As}_{\mathrm{Se}}$ to be introduced in ZnSe after the crystal is grown. Since the arsenic dopants are not introduced at high temperatures, as in bulk crystal-growth techniques, or at a growing surface, as in epitaxial crystal-growth techniques, but are introduced in bulk ZnSe at a temperature under investigator control, experiments can be designed to probe arsenic doping in ZnSe in additional ways. The introduction of $\mathrm{As}_{\mathrm{Se}}$ is an important property of this technique, since $\mathrm{As}_{\mathrm{Se}}$ is thought to be the center responsible for the observed shallow level due to arsenic doping in ZnSe, and since recent theoretical work suggests that centers other than isolated arsenic dopants at selenium sites may contribute to compensation mechanisms in ZnSe. Also, the question can be resolved as to whether the deep levels, consistently observed in ZnSe at high arsenic doping concentrations, result from the nature of the isolated $\mathrm{As}_{\mathrm{Se}}$ dopant or from interactions present during crystal growth. These interactions include arsenic dopants interacting with lattice defects and arsenic dopants interacting with other arsenic atoms.

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