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Coupling of codoped In and N impurities in ZnS:Ag: Experiment and theory

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A vapor-phase-grown epitaxial ZnS:Ag layer simultaneously codoped with In and N on GaAs substrate exhibited a 436-nm light emission and p-type conduction with a low resistivity. X-ray photoemission spectroscopy revealed that the In 3d3/2 electron binding energy of the codoped ZnS:In,N layer was smaller by 0.5 eV than that of the ZnS:In independently doped layer, although the 2p3/2 electron binding energies of Zn and S of the codoped layer agreed well with those of the independently doped layer, respectively. The reduction of binding energy was ascribed to an increase in the electronic relaxation energy for core-hole states in photoemission and reflects a large charge transfer between the In and N atoms at the first neighbor sites through covalent sp3 bonding orbitals. An increase of the spectral intensity at around 4 eV relative to the valence band maximum observed for the codoped layer corresponds to a new state at −3.67 eV from the valence band maximum due to a strong coupling between the In 5s and N 2p orbitals at the first neighbor sites, derived from a first-principle band structure calculation for ZnS:(In,2N).

INTRODUCTION

In the past decade Zn chalcogenides with direct band gap have been drawing considerable interest with the expectation of realizing light emitters in the green to blue portion of the spectrum.1–6 ZnS has a wide band gap of approximately 3.7 eV at room temperature. Low resistivity ZnS layers with n- and p-type conduction were fabricated by the vapor phase epitaxial method on GaAs substrate.7–10 Doping of appropriate impurities enable the blue emission is important for light emitting device application. It is well known that the blue-Ag emission is due to Ag impurity substituting the Zn site of ZnS.11,12 The blue-Ag emission with low-resistivity p-type conduction has been reported for the In and N simultaneously codoped ZnS:Ag layer by vapor phase epitaxy.13 Here we report the electronic structure of the In and N codoped ZnS:Ag layer examined by x-ray photoemission spectroscopy (XPS).

EXPERIMENT

Epitaxial layers of ZnS with a thickness of approximately 1 μm were grown at 610 °C on a GaAs (100) surface by H2 gas flow using a luminescence grade unactivated ZnS powder source. For introducing the blue-Ag centers, Ag metallic powders (purity of 99.99%) were used as the source of Ag impurity. For the doping of In and N to the epitaxial ZnS:Ag layer, metallic In (purity of 99.99%) and NH3 gas (purity of 99.9%) were used as the sources. A ZnS:In layer was also prepared as a reference for XPS. Preparation conditions were similar to those described in Ref. 13.

For the In and N codoped ZnS:Ag layer, the lattice constant a of the cubic lattice from the (400) reflection was 0.5403 nm by x-ray diffraction measurement. Hall effect measurement by the van der Pauw method of the sample revealed that the conduction type was p-type, the hole concentration was (0.56–1.4) × 1019 cm–3, and the mobility was 11–25 cm2/V s.13,14 The p-type conduction was reconfirmed by Seebeck effect measurement. An intense 436-nm emission corresponding to the blue-Ag emission was seen in the photoluminescence spectra excited with the Hg 313- or 365-nm lines measured at 77 K. The 436-nm emission was due to donor–acceptor pair type recombination judging from a blueshift of the line with increasing the excitation intensity.14

X-ray photoemission spectra were measured with a Surface Science Laboratories SSX-100 spectrometer using monochromatized Al Kα radiation in vacuum pressure less than 6 × 10–10 Torr at room temperature. The solid angle of the input lens of the energy analyzer was 30° and the probing area was 300×500 μm2 on the sample surface. The spectrometer was calibrated by using the Au 4f7/2 (84.0 eV) electrons. The pass energy of the spectrometer was set to 50 eV and the full width at half maximum (FWHM) of the Au 4f7/2

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peak was 1.03 eV. The estimated electron energy uncertainty was ±0.15 eV in this experiment.

RESULTS AND DISCUSSION

Usually, in XPS the observed spectral features are labeled in terms of one-electron quantum numbers, however, photoemission from a solid is evidently a many-body process since the motion of each electron cannot be independent of the motions of other electrons. It is generally stated that the actual photon absorption process occurs nearly instantaneously (≈10⁻¹⁷ s) and the hole switching occurs in a time less than 10⁻¹⁶ s. The localized screening response (10⁻¹⁶–10⁻¹⁵ s) is very fast in contrast to the delocalized screening response (10⁻¹³–10⁻¹² s). Delocalized screening is accompanied with core–valence–valence (CVV) Auger transitions. Negative charge flows towards the photohole in order to screen the suddenly created positive charge. Relaxation energy (R), lowering the observed binding energy (E_b) of the photoelectrons than that expected from Koopmans’ theorem, is the result of this flow of negative charge. The E_b of a level j, E_b(j), is the difference in the total energy of the system in its ground state and in the state with one electron missing in the orbital j. This can be expressed as

$$E_b(j) = -\epsilon(j) - R(j).$$

Here, \(\epsilon(j)\) is the orbital energy and \(R(j)\) is the relaxation energy.\(^{17}\) The relaxation energy varies with changes in chemical and physical states, therefore the \(E_b\) shift can be written as \(\Delta E_b(j) = -\Delta \epsilon(j) - \Delta R(j)\). For most situations encountered in XPS, the equation is close enough to discuss the chemical shift.\(^{18}\) So, we can examine the co-doping effects of In and N on the electronic structure by XPS.

The core levels and valence band spectra were measured for the samples of the In and N codoped ZnS:Ag layer (ZnS:In,N)\(^{19}\) and the In doped ZnS layer (ZnS:In). The ZnS:In,N and ZnS:In samples were conductive. The Zn 2p\(^{3/2}\) and S 2p electron E_b’s were 1022.0 and 162.1 eV, respectively. They agreed well with each other within the statistical uncertainty for the samples. The electronic structure of the ZnS matrix was scarcely affected by the manner of doping of In and N.

For the ZnS:In,N sample, both the In 3d and N 1s electron spectra were observed clearly as shown in Figs. 1 and 2. The In 3d\(^{5/2}\) electron E_b of the ZnS:In,N sample was smaller by 0.5 eV than that of the ZnS:In sample. The In 3d\(^{5/2}\) electron E_b was lowered by the simultaneous codoping of In and N. In the case of substitutional doping of the In\(^3+\) to Zn\(^2+\) lattice site, the formal valence of In\(^3+\) is invariant with the manner of doping (codoping or not). As described before, an E_b shift (\(\Delta E_b\)) can be portioned into two terms (\(\Delta \epsilon\) and \(\Delta R\)). The \(\epsilon\) (orbital energy) should not vary with the manner of doping to the ZnS matrix, though the \(R\) (relaxation energy) should vary with the manner of doping. The energy \(R\) reflects a degree of the core–hole screening by flows of valence electrons through the \(sp^3\) covalent bonds between the cation and anion sites. It is readily understood that codoped In\(^3+\) and N\(^3–\) ions at the nearest neighbor sites (ZnS:In,N sample) enlarge the \(R\) value for both In and N atoms by charge transfer via In–N sp\(^3\) covalent bonds. In the ZnS:In sample, independently doped electrons (In\(^3+\) to Zn\(^2+\) site) lessen the \(R\) value for an In atom because of a decrease in covalency of the In–N sp\(^3\) bonds. From the octet electron configuration for the Zn–N sp\(^3\) bond, the excess electrons at the Zn site should enter into the antibonding orbitals, therefore the excess electrons weaken the Zn–N sp\(^3\) covalent bonds. Larger and smaller \(R\) values correspond to well-screened and poorly screened core–hole states, respectively. The well-screened and poorly screened core–hole states cause narrowing and broadening of the core–electron spectra, respectively, as seen in Fig. 1. The FWHM of the In 3d\(^{5/2}\) peak of the codoped ZnS:In,N sample was smaller than that of the independently doped ZnS:In sample. Therefore the codoping effect of In and N is an enhancement of donor–acceptor coupling in the ZnS matrix. So, it is expected that the detailed structure of the valence band, especially at the higher E_b side mirroring the covalent s–p bonding orbitals, differs from each other with the manner of impurity doping.

Quadric background subtracted valence band spectra are shown in Fig. 3. The valence band spectra showed a two-peaked (A and B) structure with the energy splitting of about 3.3 eV. The ZnS:In,N sample showed an enlargement of relative intensity in the vicinity of region B (≈4 eV relative to the valence band maximum). As mentioned above, the codoped In and N at the first neighbor sites can form covalent sp\(^3\) bonding orbitals, and then add a new density of states (DOS) to that of the ZnS matrix, though the indepen-
and S sites, respectively, should result in an increase of the translation. The outermost calculation using the augmented spherical wave method with spectra of the samples. Around B is what is expected from the analyses of core-level the antibonding orbitals. Therefore the increased intensity at valence band since the delivered excess electrons enter into the ZnS matrix when the atoms were simultaneously incorporated into the matrix.

In order to clarify the codoping effect of In and N with ZnS we have carried out a first-principle band structure calculation using the augmented spherical wave method with the local density treatment of electronic exchange and correlation. The outermost s, p, and d orbitals of Zn and S atoms, and the outermost s and p orbitals of In and N atoms were employed as valence electrons. Under periodic boundary conditions, supercells containing 64 atoms were generated. One of the 32 sites of Zn atoms was replaced with an In site for ZnS:In. For ZnS:(In,2N) of the molar ratio of In:N=1:2, at first we replaced one of the 32 sites of S atoms with a N site and one of the 32 sites of Zn atoms with an In site to determine the structure minimizing the total energy of ZnS:(In,N) of the molar ratio of In:N=1:1, and then one of the remaining 31 sites of S atoms was replaced with another N site. Eventually, the cluster structure of N–In–N positioning the first neighbor sites was favorable in the total energy calculations. The calculation is described elsewhere in detail.20 The sp bonding of In and N atoms locating at Zn and S sites, respectively, should result in an increase of the DOS in the valence band. Figures 4(a) and 4(b) show the calculated DOS of the In and N codoped ZnS and that of the In doped ZnS, respectively. For comparison with the experimental spectra, the zero-energy points of the DOS were aligned at the valence band maximum since the conduction type of the In and N codoped ZnS was p-type and that of In doped ZnS was n-type in the calculation. The calculated DOS showed the two-peaked structure above ~5.61 eV. The energy splitting between the two (C and D) peaks in the calculation amounted to 3 eV. The calculated splitting agrees well with that of the experiment (3.3 eV). A prominent feature in the calculated DOS of the In and N codoped ZnS is a new state denoted by the arrow at ~3.67 eV due to In s–N p σ bonding. The calculated feature agrees well with that observed in the experiment. It has become clear that the codoped In and N atoms form InN-like bonding state locally in the ZnS matrix when the atoms were simultaneously incorporated into the matrix.

It is readily understood that in photoemission the In core–hole states of the ZnS:In,N and ZnS:In samples undergo delocalized screening by electrons within the valence band, and the electronic relaxation energy of the codoped ZnS:In,N sample and that of the independently doped ZnS:In sample differ from each other since the dielectric constant at around the doped In site varies with the manner of doping. The codoped In and N atoms occupy the Zn and S positions, respectively, at the first neighbor sites in the ZnS matrix. Therefore the dielectric constant at around the In atoms in the ZnS:In,N sample should be close to that of InN. The In atoms of the ZnS:In sample substitute the Zn sites, so the dielectric constant at around the In atoms in the ZnS matrix should be the same as that of ZnS. It is well known that the bond of ZnS (ε=5.1) is more ionic than that of InN (ε=9.3), and in ionic crystals the polarization energy of an ion is given by the equation \( E_{\text{pol}} = (-1/2r)[1 - (1/\varepsilon)] \) in atomic units.21 Where r is the effective hole radius and ε is the dielectric constant at optical frequencies. \( \Delta R = \Delta E_{\text{pol}} \) can be assumed in the photoemission relaxation process of crystals with ionic bonds. So, we obtain the expression \( \Delta R(ZnS:In\rightarrow ZnS:In,N) = (-1/2r)[(1/\varepsilon_{InN}) - (1/\varepsilon_{ZnS})] \). The values of \( \varepsilon_{InN} \) and \( \varepsilon_{ZnS} \) were mentioned above. The value of r is 1.25 Å, which is the In 5s orbital radius. Thus we have the following result: \( \Delta R(ZnS:In\rightarrow ZnS:In,N) = 0.51 \) eV, which is in good agreement with the experimental \( \Delta E_b \) (0.5 eV). The codoped In results in delocalization of the N acceptor state accompanying a low-resistivity p-type conduction, and then enhancing the donor–acceptor type recombination for the 440-nm emission of ZnS:Aga.
SUMMARY

XPS of the ZnS:In,N and ZnS:In samples revealed that the In and N codoping effect for ZnS:Ag is an enhancement of donor–acceptor coupling in the ZnS matrix. The highly covalent In–N $sp^3$ bond, formed between the In and N atoms at the first neighbor sites in the ZnS matrix by the codoping, brought about the enlargement of $R$ by 0.5 eV and an increase of the spectral intensity at around 4 eV relative to the valence band maximum. The feature of the valence band spectrum can be predicted by that of the DOS from a first-principle band structure calculation; strong interaction between the In $s$ and N $p$ states forms a new DOS located at $-3.67$ eV from the valence band maximum, and it gives the larger dielectric constant which screens well the hole states in both the core and valence levels.

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14 S. Kishimoto (unpublished).
18 In the XPS of the In and N codoped ZnS:Ag layer we could not find any signals from the Ag impurity, so hereafter we denote nominally the sample as ZnS:In,N.