

Vacuum ultraviolet reflectivity measurements of thin-film electroluminescent phosphors

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Vacuum ultraviolet reflectivity measurements of three thin-film electroluminescent phosphors, zinc sulfide (ZnS), strontium sulfide (SrS), and strontium-calcium thiogallate ($\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ga}_2\text{S}_4$), are reported using thin-film samples. Measured ZnS reflectivity peak positions are in agreement with values previously reported in the literature. SrS room temperature reflectivity measurements are found to be consistent with previously reported low temperature measurements. Reflectivity measurements of $\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ga}_2\text{S}_4$ are reported for the first time; the reflectivity spectrum is found to rise monotonically above the band gap and to exhibit almost no structure, except for a small shoulder at ~ 6.8 eV and a single, broad peak at ~ 8.5 eV. The unusual nature of the $\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ga}_2\text{S}_4$ reflectivity spectrum is attributed to positional disorder in the stoichiometric thiogallate film. © 1996 American Institute of Physics. [S0003-6951(96)00749-8]

Vacuum ultraviolet (VUV) reflectivity measurements are often used to determine the reflectivity spectrum and to assess the critical point energies of semiconductors and insulators.^{1,2} The measured reflectivity spectrum and critical point energies then provide an experimental data base upon which an energy band structure calculation (e.g., empirical pseudopotential method) may be performed.² Typically, VUV reflectivity measurements are performed^{3,4} using single crystal samples which are cleaved (often *in situ* in ultrahigh vacuum) in order to minimize the amount of contamination and structural imperfection at the surface. Although cleavage of single crystal samples in ultrahigh vacuum is the ideal way to prepare a sample for VUV reflectivity measurements, such an experimental procedure is not always convenient since a single crystal substrate is not always readily available.

The work described herein is motivated by our interest in modeling high-field transport in thin-film electroluminescent (TFEL) phosphors.^{5,6} Specifically, we are interested in modeling high-field transport in strontium or calcium thiogallates (SrGa_2S_4 and CaGa_2S_4) or the quaternary alloy of these two ternary alloys. Other than the energy band gap of these materials, we are aware of no band structure information for these materials.^{7,8} Also, single crystals of these materials are not available to us whereas thiogallate thin films are deposited on a routine basis. Therefore, the purpose of the work described herein is to perform VUV reflectivity measurements of thiogallate thin films in order to provide an initial data base for future band structure calculations. Furthermore, in order to confirm the viability of our experimental procedure, our initial VUV reflectivity measurements are performed using ZnS and SrS. ZnS is the most common TFEL phosphor material and its VUV spectrum and critical

point energies are known.⁹⁻¹⁴ SrS is the second most common TFEL phosphor material and its VUV spectrum has been assessed previously, but only at low temperature.^{3,4}

The VUV measurements are performed at the Army Research Laboratory, Fort Monmouth, New Jersey, using a McPherson dual monochrometer VUV reflection/transmission measurement system with a deuterium source and operated at high vacuum ($< 1 \times 10^{-5}$ Torr). All VUV measurements are performed at room temperature. It should be noted that the VUV reflectivity spectra are obtained from taking a difference between reflectivity spectra of a sample and of a mirror replacing the sample (the mirror spectrum is obtained in order to determine the overall system response). We find¹⁵ that the accuracy of the $\sim 7-8$ eV portion of the reflectivity spectra is strongly dependent on precisely maintaining the angle of reflectance alignment of the sample and the mirror. Although great care is taken to minimize this misalignment problem, it is impossible to ensure that there is no misalignment. Thus, the detailed features of our reflectivity spectra in the $7-8$ eV range should be interpreted with some caution.

The VUV reflectivity spectrum of a ZnS thin film (deposited at Planar Systems by evaporation) is shown in Fig. 1. Because this is a thin-film sample, a distinct set of Fabry-Perot oscillations due to interference is clearly evident below the band gap. In fact, the ZnS band gap energy is deduced to be 3.7 eV from Fig. 1 by noting where the onset of the Fabry-Perot oscillations are extinguished. Two dominant peaks at 5.7 and 7.5 eV are seen in Fig. 1 and a shoulder is also evident at 7.0 eV. Previous workers have reported the 5.7 eV peak energy at 5.79,⁹ 5.78,¹⁰ 5.73,¹¹ 5.7,¹² and 5.74 eV;¹³ the 7.0 eV peak energy at 6.99,⁹ 7.02,¹⁰ 7.00,¹¹ ~ 6.9 ,¹² and 7.00;¹³ and the 7.5 eV peak energy at 7.41,⁹ 7.5,¹⁰ and

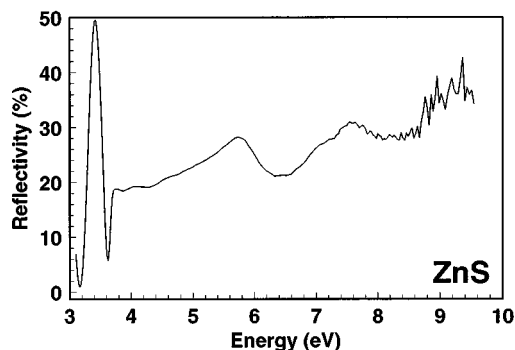


FIG. 1. Reflectivity spectrum of a ZnS thin film.

~ 7.5 eV.¹² Thus, our measured peak locations are in agreement with those reported by other workers who employ single crystal substrates and perform their experiments under better-controlled conditions (in terms of the condition of the surface). However, there are some differences between the peak shapes and relative peak heights that we measure compared to those reported in the literature. Other workers find the 7.0 eV feature to be a well-defined peak whereas we observe this feature to be more of a shoulder. Also, the 7.5 eV feature is found to be a peak by certain researchers⁹ and a shoulder by others.^{10,12} Some of the 7–8 eV differences between our measured ZnS reflectivity spectra and those measured by other workers are undoubtedly associated with the misalignment problem discussed previously. The 5.7 eV peak is a critical point energy which is attributed¹⁴ to $L_{3v} - L_{1c}$ and $\Delta_{5v} - \Delta_{1c}$ transitions while the 7.5 eV peak is attributed¹⁴ to $\Delta_{5v} - \Delta_{1c}$ transitions. The 7.0 eV peak is attributed to $\Delta_{5v} - \Delta_{1c}$ transitions. In addition to the 5.7, 7.0, and 7.5 eV features seen in Fig. 1, there is some evidence for another peak at >9 eV. It is difficult to determine the actual energy position of this peak since the system response is very weak at energies above ~ 9 eV. Other workers have reported fairly broad peaks at 9.78,⁹ 9.6,¹⁰ and ~ 9.0 eV¹² that may correspond to our >9 eV peak.

The VUV reflectivity spectrum of a SrS thin film (deposited at the Heinrich–Hertz Institut by multisource deposition) is indicated in Fig. 2. From the extinction of the Fabry–Perot oscillations, the SrS band gap is estimated to be 4.5 eV, in reasonable agreement with that reported⁴ in the literature (i.e., 4.3 eV). Additionally, the SrS reflectivity

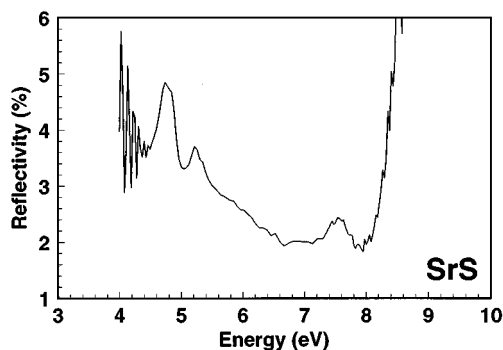


FIG. 2. Reflectivity spectrum of a SrS thin film.

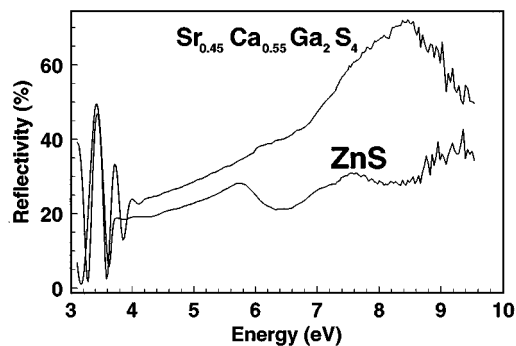


FIG. 3. Reflectivity spectra of a ZnS and a $\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ga}_2\text{S}_4$ thin film.

spectrum shown in Fig. 2 possesses three primary peaks centered at 4.8, 5.3, and 7.7 eV. Note that there is some structure present in the 4.8 and 5.3 peaks shown in Fig. 2. VUV measurements performed at 2 K using synchrotron radiation and single crystal samples cleaved in ultrahigh vacuum reveal⁴ that these are indeed exciton doublet peaks which are located at 4.761, 4.855, 5.321, and 5.425 eV; also, measurements performed at 77 K reveal³ a small peak at ~ 7.8 eV. Although our measurements cannot be directly compared to those of Refs. 3 and 4 because our measurements are obtained at room temperature while their measurements are obtained at 2 and 77 K, respectively, the reasonable agreement between the low temperature peak energies^{3,4} and our energies and the excellent agreement in the general shape of the reflectivity spectra reported in Ref. 3 (i.e., see Fig. 3 of Ref. 3) and our data provide us with confidence that the general trends which we measure for SrS are reasonable.

It is important to note that even though our ZnS and SrS samples are polycrystalline thin films which are exposed to atmosphere for an extended period of time, our measured critical point energies are in excellent agreement with previously reported values which are obtained from VUV reflectivity measurements performed using single crystal substrates and minimizing surface contamination and surface structural imperfection by cleaving the sample, often in ultrahigh vacuum, just prior to loading the sample into the VUV spectrometer. These results provide us with some verification of the experimental viability of our procedure so that we can confidently perform measurements on thiogallates which have never before been measured.

The VUV reflectivity of a $\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ga}_2\text{S}_4$ thin film (deposited at Planar Systems by sputtering and crystallizing via a postdeposition heat treatment at 800) is shown in Fig. 3; The ZnS reflectivity of Fig. 1 is also indicated in Fig. 3 for comparative purposes. From the extinction of the Fabry–Perot oscillations, the $\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ga}_2\text{S}_4$ band gap is estimated to be 4.2 eV, in agreement with that reported⁸ in the literature for CaGa_2S_4 (i.e., 4.2 eV) and SrGa_2S_4 (4.4 eV). In contrast to ZnS and SrS, the reflectivity spectra of $\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ga}_2\text{S}_4$ rises monotonically above the band gap and exhibits very little structure with a slight shoulder at ~ 6.8 eV and a broad peak at ~ 8.5 eV. Note also that reflectivity above the band gap of the $\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ga}_2\text{S}_4$ thin film is much stronger than that found for ZnS or SrS.

At energies above the band gap, a reflectivity spectrum reveals the strength and structure of the joint density of states

(i.e., the combined density of filled valence band states from which electrons originate and empty conduction band states which are the final states into which the electrons find themselves after photon absorption occurs). Note that the reflectivity spectra, which reflects the joint density of states, are dramatically different for the three TFEL phosphor materials studied. The ZnS joint density of states exhibits a rather flat background with several well-defined peaks; this type of structure is typical of “covalent” group IV, III–V, or II–VI semiconductors. The ZnS spectrum is characterized as slowly rising just above the band gap with two well-defined peaks occurring at 2 and 3.3 eV above the band gap and a shoulder at 2.7 eV. The SrS joint density of states is distinctly different than that of ZnS in the energy regime with the largest joint density of states distinguished by the two well-defined exciton peaks which occur at 0.3 and 0.8 eV above the band gap; note that the joint density of states then decreases monotonically from 1 to 2.8 eV above the band gap. The SrS reflectivity spectrum is typical of ionic materials such as alkali halides and titanates. In contrast to both ZnS and SrS, the $\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ga}_2\text{S}_4$ joint density of states increases monotonically with very little structure up to ~ 4.1 eV above the band gap. The lack of structure of the reflectivity spectrum of the $\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ga}_2\text{S}_4$ thin film is quite unusual. We suspect that this lack of structure may be evidence that these thiogallate films possess a significant amount of positional disorder¹⁶ even though they are stoichiometric. Positional disorder in these materials seems feasible when it is recognized that the crystal structure of these thiogallates is orthorhombic with 224 atoms per unit cell.⁷

The reflectivity trends measured for these three TFEL phosphors provide clues regarding the relative TFEL performance of these three phosphors. Monte Carlo simulation of the high-field transport in ZnS indicates^{5,6} that the conduction band density of states is the most important factor in determining the extent of electron heating and, hence, the expected TFEL efficiency of the phosphor. If the reflectivity trends shown in Figs. 1–3 are primarily due to the conduction band density of states, it is expected that the high-field transport properties (and presumably the TFEL performance, at least to the extent to which it is determined by the transport) of SrS would be superior to that of ZnS or thiogallates since a monotonically increasing conduction band density of states with increasing energy provides an efficient means of cooling the electron distribution. Further bandstructure work

is required to determine to what extent the measured reflectivity spectra of SrS and thiogallates are representative of the conduction band density of states.

In summary, VUV reflectivity measurements of ZnS, SrS, and $\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ga}_2\text{S}_4$ thin films are performed. The measured ZnS peak energies are in agreement with values published in the literature. The SrS peak energies and general shape of the reflectivity spectrum are consistent with low temperature reflectivity measurements. The VUV reflectivity spectrum of $\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ga}_2\text{S}_4$ is found to be almost structureless and monotonically increasing up to ~ 8.5 eV; the unusual nature of the measured reflectivity spectrum is attributed to positional disorder in thiogallate thin films. These reflectivity results suggest that the bandstructure of these sulfides, and hence presumably their transport properties, are very different.

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