X-ray photoelectron spectroscopy valence band data for ZnS, SrS, and Sr$_{0.45}$Ca$_{0.55}$Ga$_2$S$_4$ luminescent thin films

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The valence band of ZnS, SrS, and Sr$_{0.45}$Ca$_{0.55}$Ga$_2$S$_4$ thin film phosphors were measured by x-ray photoelectron spectroscopy. The valence band spectrum from polycrystalline ZnS film compared favorably with that previously reported for ZnS single crystals, and with calculated theoretical densities of states (after convolution with a Gaussian curve). The SrS valence band spectrum exhibited three peaks, which generally agree with the expected densities of states. The Sr$_{0.45}$Ca$_{0.55}$Ga$_2$S$_4$ spectrum features were much less intense, consistent with the film being amorphous. © 1998 American Vacuum Society. [S0734-2101(98)03202-3]

I. INTRODUCTION

There is much interest in phosphors used in flat panel displays (FPD), particularly on films prepared for field emission displays. It is well known that films have lower brightness and efficiency than powders, and it is necessary to improve these characteristics in order to develop FPD with good performances. Also, it is well known that phosphors degrade under electron bombardment.\textsuperscript{1} Therefore, it is important to understand the phenomena occurring during the degradation. Recently Swart \textit{et al.}\textsuperscript{1} proposed a new mechanism to explain the degradation of a ZnS powder, consisting of: (1) decomposition of the residual vapor molecules (water, hydrogen, methane, carbon monoxide, and carbon dioxide) in the vacuum environment by the electron beam, and (2) subsequent chemical reactions of the atomic species with the surface of the phosphor. As a result of this process, a nonluminescent layer is formed on the material and the brightness is lowered. Since these phenomena occur at the surface, it is clear that surface characterization techniques should be the best tool to investigate them. X-ray photoelectron spectroscopy (XPS) is a surface technique sensitive to chemical changes, which makes it an excellent candidate to perform this analysis.

One of the capabilities of the XPS technique is to analyze the low binding energy region (0–30 eV typically), i.e., the valence band of the material. XPS studies of the valence band have proven to give unique and complementary information.\textsuperscript{2} Also, since theoretical calculations of band structures are available for many compounds [and the density of occupied states (DOS), as well], it is possible to make comparisons between theoretical DOS and the XPS results. In contrast, the intensity of the valence-band XPS signal is weaker than the intensity of the signal coming from the core levels. This is due to the photoelectric cross section, which is weaker than the intensity of the signal coming from the core levels. As a result of this process, a nonluminescent layer is formed on the material and the brightness is lowered. Since these phenomena occur at the surface, it is clear that surface characterization techniques should be the best tool to investigate them. X-ray photoelectron spectroscopy (XPS) is a surface technique sensitive to chemical changes, which makes it an excellent candidate to perform this analysis.

In this work we report XPS measurements in the valence band region of ZnS, SrS, and Sr$_{0.45}$Ca$_{0.55}$Ga$_2$S$_4$. The purpose is to provide a basis to monitor the degradation of the samples in further investigations by following the evolution of their valence-band XPS spectra.

The ZnS and SrS are two of the most studied phosphors. XPS measurements in the valence band region of ZnS crystals have been reported previously.\textsuperscript{3} A comparison of our measurements with these previous results provide us with some verification of the reliability of our procedure; this is important because no XPS measurements in the valence band region or DOS calculations for SrS or Sr$_{0.45}$Ca$_{0.55}$Ga$_2$S$_4$ have been reported.

II. EXPERIMENTAL PROCEDURE

The ZnS thin film was deposited at Planar Systems, Beaverton, OR, by evaporation. The SrS film was grown at the Heinrich–Hertz Institut, Berlin, Germany, by multisource deposition, and the Sr$_{0.45}$Ca$_{0.55}$Ga$_2$S$_4$ sample was deposited at Planar Systems by sputtering and heat treated at 800 °C after deposition. Valence band measurements of ZnS, SrS, and Sr$_{0.45}$Ca$_{0.55}$Ga$_2$S$_4$ films were taken with a Perkin Elmer PHI 5100 ESCA system, using an achromatic Mg K$_\alpha$ (1254 eV) x-ray radiation with a power of 300 W. The measurements were made in an UHV chamber with a background pressure of 10$^{-9}$ Torr. We used a pass energy of 17.9 eV. The data acquisition time was 27, 120, and 149 min for ZnS, SrS, and Sr$_{0.45}$Ca$_{0.55}$Ga$_2$S$_4$, respectively. We only sputtered the SrS sample. The background from inelastically scattered electrons was assumed to be linear in the analyzed region and subtracted. Because of the nonmonochromaticity of the x-ray source, satellites from close core levels interfere with the valence band signal. Two Gaussian curves were fitted to reproduce the K$_\alpha_1$ and K$_\alpha_4$ signals associated to the 3d peak in the XPS spectrum of a silver foil. We used the same separation, relative intensities, and linewidths proportional to that of the main photopeaks in our spectra, to subtract two Gaussian curves corresponding to the satellite signals present in the valence band region.

Since the films were not conducting, all samples were charged when irradiated by the x-ray beam. To determine the...
position of the Fermi level ($E_F$), we took the position of the adventitious carbon peak C ($1s$) at 284.6 eV as a reference. This procedure to localize $E_F$ of nonconducting materials is not free of errors; however, it is still the most common method to correct charge shifting. $E_F$ and all binding energies were referred to the top of the valence band (TVB), which was determined by extrapolating the steep leading edge of the highest valence-band peak to the baseline. The TVB was labeled as the zero-energy level.

Broadening is another important effect to consider in XPS measurements of the valence band, and it is important to take into account its effect on the edges of the valence band (particularly the TVB) to estimate the correct position of $E_F$. There are several sources for the broadening of peaks in an XPS spectrum. Two important contributions are the lifetime of the excited state, and instrumental broadening. To account for the instrumental contribution, we convoluted the theoretical DOS of ZnS sample with a Gaussian having the same full width at half-maximum, or FWHM, of the closest core level. The band gap of these films was estimated from optical reflectance data reported by Lite et al.\textsuperscript{6}

III. RESULTS AND DISCUSSION

A. ZnS

The C ($1s$) peak indicated a charge shift of 2.6 eV in the ZnS spectrum. In Fig. 1 we present the original XPS spectrum in the region 0–20 eV, the spectrum after subtraction of the background, and the two Gaussian curves adjusted to represent the satellite peaks coming from the Zn 3$d$ core level. The resulting valence band XPS spectrum after subtraction of the background and the satellites, and taking the TVB as the origin is presented in Fig. 2. Three main peaks (I, II, and III), and one shoulder ($S_1$) are distinguished in this spectrum. Peak III is located slightly below the Zn 3$d$ peak. Table I shows the positions of these features (relative to TVB) for our sample and for a ZnS single crystal, as reported in Ref. 3. The present ZnS spectrum and that obtained from a single crystal are very similar.

The DOS was calculated using the $kp$ method by Li et al.\textsuperscript{7} We convoluted the DOS with a Gaussian curve of FWHM = 1.25 eV. This value corresponded to the FWHM of the Zn 3$d$ core level of the XPS spectrum, and represented the instrumental broadening. In Fig. 3 we show the theoretical curves (before and after convolution) and the XPS result over the region 0–6 eV (the high-energy side was extrapolated to the baseline). We fit the position of peak I by shifting the XPS spectrum accordingly.

We observed a good agreement of the position of shoulder $S_1$ between the experimental curve and the original DOS; however, we found that the agreement for peak II was not as good. We can see that the relative intensities of peaks I and II in the convoluted curve fit better with the experimental result. Also, tails in both sides of the convoluted curve coincide very well with the edges of the XPS spectrum. Particularly, the low-energy tail extended to about 1.1 eV above TVB of the original DOS.

After correcting the charge shift, $E_F$ was located 1.5 eV above the experimental TVB, and this position is also shown in Fig. 3. Taking into account the broadening effect, we can conclude that the real position of $E_F$ is 2.6 eV above TVB. Since the band gap of the ZnS film is 3.7 eV (from reflectivity measurements\textsuperscript{6}), therefore $E_F$ must be located only 1.1

<table>
<thead>
<tr>
<th>XPS feature</th>
<th>Film (this work)</th>
<th>Crystal (Ref. 3)</th>
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<tbody>
<tr>
<td>I</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>$S_1$</td>
<td>3.1</td>
<td>3.2</td>
</tr>
<tr>
<td>II</td>
<td>4.7</td>
<td>4.9</td>
</tr>
<tr>
<td>III</td>
<td>11.9</td>
<td>12.4</td>
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eV below the bottom of the conduction band ($E_c$). It is worth mentioning here that according to Bringuier, $E_F$ of ZnS samples must be located 0.9 eV below $E_c$ to explain the mechanism of electroluminescence in this material. This is consistent with our estimation of the $E_F$ position.

We can conclude that our results for the present polycrystalline ZnS film correspond well with previous results (XPS for a single crystal, and predicted the $E_F$ position). This provides us with a verification of the validity of our experimental procedure (e.g., the satellites subtract) and confidence to do a similar analysis to the other two samples.

### B. SrS

The spectrum from the SrS film exhibited a 2.6 eV charge shift. It was necessary to subtract the x-ray satellites peaks resulting from the Sr 4$p$ level, located at about 19 eV. Cubic binary semiconductors in general have similar band structures. Particularly, the SrS band structure has many similarities to ZnS; for example, four valence bands are formed in both cases. Therefore, one would expect the shape of their XPS valence band spectra to be similar. In Fig. 4(a) we show the XPS spectrum of SrS referred to as TVB, after subtraction of a linear background and satellite signals. We found peaks I, II, and III similar to those formed in the ZnS spectrum. However, shoulder $S_1$ was not well defined in the SrS case. Peaks I, II, and III in the SrS spectrum, Fig. 4(a), were located at 2.4, 5.0, and 10.3 eV, respectively. Peak III can be associated to the fourth valence band as calculated by Kaneko and Koda. Additionally, an unexpected peak was found at about 11.8 eV. We sputtered the sample with Ar$^+$ ions for 5 min, and the resulting spectrum is shown in Fig. 4(b). The peak at 11.8 eV was not present anymore, therefore this could be originated from contaminants on the surface. However, peak II also disappeared, most likely as a consequence of ion-induced damage in the surface.

After correcting the charging shift of the spectrum, $E_F$ of SrS was located only 0.2 eV above TVB. Since there are no calculations of DOS available, we could not follow the same procedure used in the case of the ZnS sample to estimate the broadening of the XPS spectrum of the SrS sample. However, if we assume that the broadening is similar for both samples (and therefore the position of $E_F$ relative to the TVB is located around 1 eV above its actual position), we can estimate that $E_F$ might be located at around 1.2 eV above TVB. Since the band gap of the SrS film is 4.5 eV (from reflectivity measurements), $E_F$ must be located 3.3 eV below the conduction band.

### C. Sr$_{0.45}$Ca$_{0.55}$Ga$_2$S$_4$

The XPS spectrum of the amorphous Sr$_{0.45}$Ca$_{0.55}$Ga$_2$S$_4$ film exhibited a 0.9 eV charge shift. While the thiogallate band structure is complicated by the fact that it is a solid solution of two ternary alloys (SrGa$_2$S$_4$ and CaGa$_2$S$_4$), the valence band should still exhibit sulfur s- and p-like behavior because sulfur is the common anion in both alloys. However, the resulting XPS spectrum after subtracting the inelastic background and the Sr 4$p$ satellites is almost featureless (Fig. 5). The signal begins at TVB and increases until it reaches a maximum at about 3.75 eV and then decreases to about 8 eV. We observed a broad peak at 9.85 eV which may be due in part to contaminant species present on the surface. No sputtering process was conducted in this sample.

$E_F$ was located at 0.1 eV above TVB, as shown in Fig. 5. Assuming that the valence band is broadened about 1 eV, one finds that $E_F$ must be located around 1.1 eV above TVB. The band gap of this sample is 4.1 eV, therefore $E_F$ must be 3 eV below the conduction band. A similar, almost featureless, spectrum was obtained for the optical reflectivity of the Sr$_{0.45}$Ca$_{0.55}$Ga$_2$S$_4$ thin film. The diffuse features of the conduction band and valence band in this sample may result from a positional disorder that smears the band features because of the disruption of the periodic potential.
IV. CONCLUSIONS

XPS measurements of polycrystalline thin films were performed in the valence band region of ZnS, SrS, and 
$\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ga}_2\text{S}_4$. For ZnS, there was a good agreement between the present study of the polycrystalline thin film and the results from a single crystal. The Fermi level position of the ZnS sample was located 1.1 eV below the bottom of the conduction band. XPS valence band spectra of SrS and $\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ga}_2\text{S}_4$ were reported. Three peaks were observed in the SrS spectrum; this was expected from band structure calculations. The $\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ga}_2\text{S}_4$ valence band spectrum revealed two broad peaks. These results provide a basis to monitor the degradation of the samples in further investigations.

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7Z. Li, G. Sanders, and C. Stanton (unpublished).