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Thickness dependence of cathodoluminescence in thin films

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Abstract. Thin-film samples are being increasingly used in high-resolution imaging studies of cathodoluminescence (CL) from materials, in order to achieve the smallest CL source possible. The analysis of luminescence signals from thin-film material is often hampered by the changes associated with variations in film thickness. This thickness effect has been analysed in a simple model which takes into account the diffusion of the excited states in thin films. The electron beam is assumed to provide a uniform excitation density over the entire film thickness appropriate to electron-transparent films. The intensity variation of the CL signal as a function the foil thickness t is given by the formula $I(t) = I_0\{t - 2L/[\coth(t/2L) + f]\}$ where L is the diffusion length of the energy carrier in a bulk sample and f is the ratio of the bulk diffusion 'velocity' L/τ to that of the surface recombination velocity s . Both physical parameters can be obtained from a plot of the CL intensity versus the film thickness. This has been applied to a wide range of materials such as $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, $\text{YAG}:\text{Ce}^{3+}$, diamond and InP. For the last two materials, the results of the analysis are consistent with those from other experiments. For phosphors with a relatively large doping of luminescent ions, the saturation effect caused by an intense excitation density must be taken into account in interpreting the physical parameters.

1. Introduction

The direct interaction volume of a focused electron beam can be reduced, from the order of a few μm in a bulk material (corresponding to the case of a scanning electron microscope (SEM)) to the order of the electron probe size (less than several nanometres) in self-supporting electron-transparent thin films (corresponding to the case of a scanning transmission electron microscope (STEM)). In thin films, the diffusion length of the excited electrons and/or holes is also limited by the non-radiative surface recombination. These two factors can reduce the generation volume for cathodoluminescence (CL) signals, thus leading to a higher spatial resolution in CL micro-analysis. This advantage has been taken up to obtain CL images of high spatial resolution (Petroff *et al* 1978, Pennycook *et al* 1980, Myhajlenko *et al* 1984, Yamamoto *et al* 1984). The disadvantage of the thin-film luminescence technique is that CL signals, both in their intensities as well as in their spectral distribution, are now highly thickness-dependent. Because a large number of specimen preparation techniques for electron microscopy (such as ion-beam sputtering, chemical etching, etc) produces thin films of varying thickness, it is difficult to avoid this complication completely. Therefore a better understanding of this thickness dependence is a prerequisite of any detailed analysis of CL signals from thin films. In this

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paper we use a simple analytical model to describe the thickness effect on the CL luminescence from various electron-beam-transparent thin films. The parameters of the model can be interpreted in terms of the physical characteristics of the materials.

2. Theoretical consideration of cathodoluminescence from thin films

2.1. Beam broadening and thin-film criteria

In passing through thin films the average energy loss experienced by a fast electron is much smaller than its kinetic energy (Raether 1980). Also most inelastic scattering is in the forward direction, which produces little deviation of the incident electrons. Therefore the path length of fast electrons in a thin film is effectively the film thickness for a normally incident electron beam. Under such circumstances the rate of energy loss per unit film thickness by fast electrons inside a film can be considered to be uniform. For simplicity, we restrict the investigation within this thin-film limit.

Before proceeding with the analysis, it is worthwhile to consider the breakdown of the thin-film approximation. As the film thickness increases accumulated multiple scatterings cause a reduction in the energy of fast electrons and a deflection of fast electrons from their original trajectories. Both lead to an increase in energy loss by the fast electrons at the exit side of the thin film. The latter is more important initially. The mean deviation angle of the fast electrons can be estimated from Lenz's expression for total inelastic scattering (Lenz 1954) with relativistic correction (ignoring spins):

$$\theta_m \approx \left(\frac{e}{4\pi\epsilon_0} \right) \frac{Z}{U} \left[\frac{\pi N t}{a^3} \ln \left(\frac{\pi^2}{e\theta_L^2} \right) \right]^{1/2} \left[\left(1 + \frac{eU}{m_0c^2} \right) / \left(1 + \frac{eU}{2m_0c^2} \right) \right]$$

with

$$\theta_L^2 = \frac{6Z^{2/3}}{43.6} \frac{e}{4\pi\epsilon_0} \frac{1}{2a_0U} \left[\left(1 + \frac{eU}{m_0c^2} \right)^2 / \left(1 + \frac{eU}{2m_0c^2} \right)^2 \right] \quad (1a)$$

which can be reduced to an adequate approximation as

$$\theta_m \approx 6.2 \times 10^{-3} \frac{Z}{U(\text{kV})} \left(\frac{Nt(\text{nm})}{a^3(\text{nm})} \right)^{1/2} \quad (1b)$$

where Z is the atomic number, a the unit cell dimension, N the number of electrons in the unit cell, t the foil thickness, and U the accelerating voltage of the incident fast electrons. The assumption that the electron loses energy linearly with the depth in the foil breaks down when its trajectory is turned through a large angle with respect to the beam direction. The thin-film criteria are defined in an arbitrary, but not unreasonable way, as the thickness for which $\theta_m < 10^\circ$. The critical film thickness is then given by

$$t_c = \left(\frac{4\pi\epsilon_0}{e} \right)^2 \frac{a^3 U^2}{\pi Z^2 N t \ln(\pi^2/e\theta_L^2)} \left[\left(1 + \frac{eU}{2m_0c^2} \right)^2 / \left(1 + \frac{eU}{m_0c^2} \right)^2 \right] \quad (2a)$$

which, approximating as before, gives:

$$t_c \approx 780(U^2(\text{kV})/Z^2) a^3(\text{nm})/N. \quad (2b)$$

This is only meant to give an order-of-magnitude estimate. For Y_2O_3 it corresponds to films less than 240 nm thick. Films with thicknesses of the order of or larger than the penetration depth of the fast electrons are considered as bulk materials, where the CL resolution is controlled by the size of the electron beam interaction volume. In between

these two thickness ranges, the CL generation volume is strongly dependent on the thickness. It is worth noting that the beam size b is

$$b \approx \left(\frac{e}{4\pi\epsilon_0} \right) \frac{Z}{U} \left[\frac{\pi N t^3}{a^3} \ln \left(\frac{\pi^2}{e\theta_f^2} \right) \right]^{1/2} \{ [1 + (eU/m_0c^2)] [1 + (eU/2m_0c^2)] \} \quad (3a)$$

which is approximately given by:

$$b \approx 6.2 \times 10^{-3} \frac{Z}{U(\text{kV})} \left(\frac{N t^3 (\text{nm})}{a^3 (\text{nm})} \right)^{1/2}. \quad (3b)$$

This differs slightly from that given earlier by Brown (1981). For Y_2O_3 at 240 nm the probe has a width of over 60 nm, which is much more than the initial focused probe size. In fact this seems to be always the case, except for very thin films (figure 1). This is significant since it means that the theoretical resolution of CL micro-analysis is strongly affected by the beam broadening for a sufficiently small probe.

2.2. Diffusion and recombination in thin films

The density of the electron-hole pairs in a thin film, $n(\mathbf{r})$, may be evaluated using a steady-state diffusion equation:

$$D\nabla^2 n(x, y, z) - n(x, y, z)/\tau = -g(x, y, z), \quad (4)$$

where D is the appropriate diffusion coefficient, τ the total lifetime of the electron-hole pairs and g the electron-hole pair generation rate. In the thin-film approximation g has been assumed to be constant along the z direction (ignoring for the moment the energy carried away by the escaping secondary electrons; Berger 1983), so its absolute value is not necessary in this study.

The simplest boundary condition at the film surfaces is that due to Shockley (1961) which states that the flux of electron-hole pairs at the surface is the product of the pair density and the surface recombination velocity, s . For a film with surfaces at planes $z = 0$ and $z = t$, where t is the film thickness, the boundary condition may be written in the form:

$$D \frac{\partial n(x, y, z)}{\partial z} = \begin{cases} -sn(x, y, z) & \text{at } z = 0 \\ sn(x, y, z) & \text{at } z = t. \end{cases} \quad (5)$$

To analyse the thickness dependence of CL intensity in thin films, only the variation in the density of excess electron-hole pairs along the beam direction is needed. With one-dimensional depth-dependent quantities $n(z)$ and $g(z)$ defined by averaging over the plane of the film (t' Hooft and van Opdorp 1986):

$$n(z) = \int n(x, y, z) dx dy \quad g(z) = \int g(x, y, z) dx dy = g_0. \quad (6)$$

Equation (4) can be reduced to a one-dimensional form (by putting $L^2 = D\tau$, L being the diffusion length of the particles) as:

$$d^2 n(z)/dz^2 - n(z)/L^2 = -g_0/D. \quad (7)$$

With the boundary conditions (5) and (6), it has a solution of the form:

$$n(z) = (g_0 L^2 / D) \{ 1 - Ls \cosh [(t - 2z)/2L] / [Ls \cosh (t/2L) + D \sinh (t/2L)] \}. \quad (8)$$

The total intensity from a film of thickness t is given by

$$I(t) = \int_0^t dz q \frac{n(z)}{\tau_r^*} = I_0 \left(t - \frac{2L}{\coth(t/2L) + f} \right) \quad \text{with} \quad I_0 = q \frac{\tau}{\tau_r^*} g_0 \quad \text{and} \quad f = \frac{D}{sL} > 0 \quad (9)$$

where $1/\tau_r^*$ is the probability that the electron-hole pairs will recombine at the luminescent centres, and q is the radiative transition quantum efficiency of the luminescence centre and can be measured for example by photoluminescence (Garlick 1966).

For a film whose thickness is much larger than the diffusion length L ,

$$I(t) \approx I_0(t - t_0) \quad (10)$$

where t_0 , the cut-off thickness, is found by extrapolating the linear relation to the zero intensity:

$$t_0 = [1/(1 + f)] 2L. \quad (11)$$

The cut-off thickness varies from zero to $2L$ as a function of increasing surface recombination velocity s , i.e., only electron-hole pairs within a distance L from the surfaces will have a chance of escaping to the surfaces. The average excitation density at a distance greater than L from the surfaces remains approximately constant within the thin-film range. For the film whose thickness is comparable to or smaller than the diffusion length, the CL intensity depends on the square of the film thickness:

$$I(t) \approx (I_0 f/2) t^2 \quad (12)$$

except in the limiting case of $s = 0$ where a linear relationship is found. The case with finite surface recombination velocity has been discussed by Pennycook (1981), where the production of electron-hole pairs falls with t as before, and in addition the number of those pairs not lost to the surface falls as t . Hence the overall luminescence intensity falls as t^2 . The excitation density is not uniform within the film and is a strong function of the distance from surfaces.

From equation (11) a lower limit on the values of the diffusion length in the thin film can be estimated. The main uncertainty is the magnitude of the surface recombination velocity. Another complication is the existence of possible surface dead layers.

Surface dead layers can have different physical nature (Evangelisti *et al* 1974); they could arise from the quenching of excitons by the electrostatic image force; or from ionisation and separation of excitons (or electron-hole pairs) in a space-charge layer; or from a surface layer which is physically distinct from the interior of thin films. If there exists a surface dead layer of width t_d , the experimental cut-off thickness is approximately given by $2(t_d + t_c)$. It is then difficult to obtain a definite value for the diffusion length, unless the width of the dead layer is known.

Finally because of the definition in (6), the one-dimensional analysis presented here is valid for both focused and defocused probes.

2.3. Possibility of thin-film interference

In the above derivation of the thickness dependence of cathodoluminescence (equation (9)), only light travelling directly from the source to the detector is considered. If the top and the bottom surfaces of a thin film are relatively flat, then light beams that have reflected successively between surfaces of the film interior may recombine coherently and produce interference.

For light emission from a point source at a depth z from the top surface of the film, the electric field at the detector, ignoring its divergence, can be described as

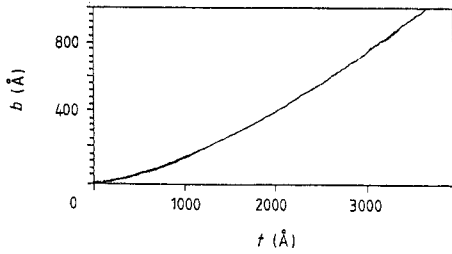


Figure 1. Estimated beam broadening as a function of thickness, calculated for Y_2O_3 . (b = probe size.)

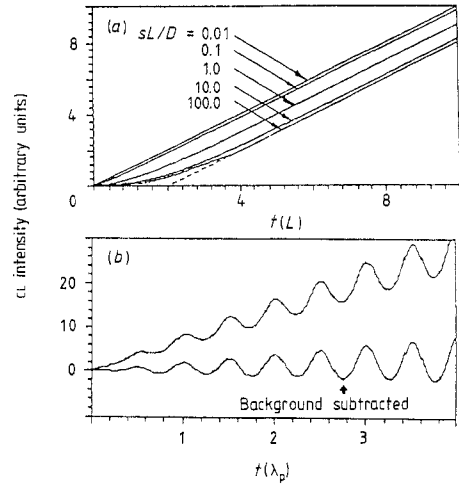


Figure 2. Calculated thickness dependence of CL in a thin film; (a) taking into account only the direct escaped light, and (b) taking into account all the reflected beams as well (for the case $s = 0$). D , L and λ are diffusion constant, diffusion length of the excitation in the solid and the wavelength of the luminescence, respectively.

$$\begin{aligned}
 E(z) &\approx E_0(z)[e^{iknz}(1 + r^2 e^{ik(2nt)} + r^4 e^{ik(4nt)} + \dots) + r e^{ikn(2t-z)}(1 + r^2 e^{ik(2nt)} \\
 &\quad + r^4 e^{ik(4nt)} + \dots)]. \\
 &\approx E_0(z)[e^{iknt}(1 - r^2 e^{ik(2nt)})](e^{-ikn(t-z)} + r e^{ikn(t-z)}). \tag{13}
 \end{aligned}$$

The first term describes the interference contribution from the forward emitting light, where r is the reflection coefficient of the light at the matter–vacuum interface of the film. The second term describes the interference contribution of the backward-emitting light, and n is the refractive index of the film. The total light emission is given by summing over the intensity contributions from all point sources along the pathlength of the fast electron in the film, which, for illustration, is calculated for the simple case of $s = 0$:

$$I(t) = I_0[(1 + |r|^2)t + (2|r|/k) \sin kn t]/(1 + |r|^4 - 2|r| \cos 2knt). \tag{14}$$

This is plotted for a light at 500 nm wavelength (appropriate for a YAG:Ce³⁺ crystal) in figure 2(b). The result shows that interference fringes are possible and can have a quite strong contrast if appropriate conditions (such as near flat surfaces) exist. Equations (13) and (14) only apply to point sources that have infinite temporal coherence. This is not true for luminescence with a finite band width. Partial temporal coherence has the effect of suppressing interference between beams with large path length differences, hence we set a limit on the number of terms to be summed in equation (13). Therefore, the amplitude of the interference contrast would not increase indefinitely with the film thickness, as the plot in figure 2(b) suggests. Because fringes occur only for film thicknesses comparable with or greater than the wavelength, the thin-film approximation upon which this section is based may also begin to break down.

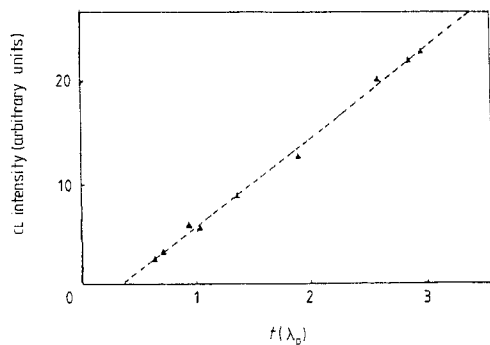


Figure 3. Thickness dependence of CL intensity observed in a commercial phosphor $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. The film thickness is expressed in terms of λ_p , the mean-free path for the valence electron excitation, which is about 210 nm.

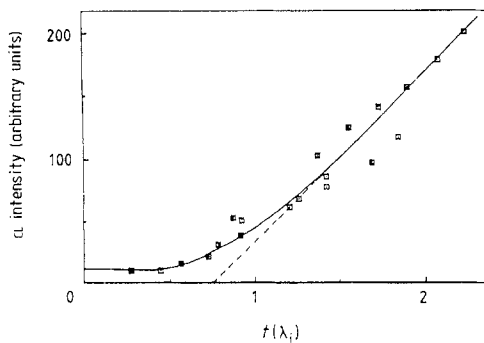


Figure 4. Thickness dependence of CL intensity observed in a commercial phosphor $\text{YAG}:\text{Ce}^{3+}$. The film thickness is expressed in terms of λ_1 , the mean-free path for the valence and shallow-core electron excitation, which is about 80 nm.

3. Experimental results

A number of materials have been examined for the thickness effect on their luminescence properties. Here we report results on thin crystals of Eu-doped yttrium sesquioxide ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$), Ce-doped yttrium aluminium garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}:\text{YAG}$) and two types of diamond.

The thin-film sample of Y_2O_3 was obtained by crushing a commercial phosphor powder (supplier: Levy West Laboratory) in acetone solution. Thin crystals of YAG were obtained by ion-beam thinning. The surface of this ion-beam-etched film is observed to be amorphous, with an estimated surface layer thickness of about 27 nm. A single crystal of diamond is etched in an oxygen flowing furnace (Evans and Phaal, 1962).

The CL experiments were carried out in a modified scanning transmission electron microscope (STEM) which has been described elsewhere (Berger *et al* 1985). Electrons were focused into a nanometre probe at the specimen plane. Intensity mapping of the CL signal was obtained from wedge-shaped thin films. The thicknesses of the films at various positions of the area covered by the map were measured by EELS or by the diffraction contrast method. From them a CL thickness dependence curve is obtained. The results are shown in figures 3–6.

The thickness dependence of CL in thin films has also been investigated by Myhajlenko *et al* (1984) for InP crystals using a scanning system in a transmission electron microscope. The probe size used was in the order of 100 nm, thus the thickness measurement was an average measurement. Their results, including those from exciton- and impurity-related luminescence are shown in figure 7.

For a thick YAG:Ce sample fringes have sometimes been observed in the CL micrograph, and are visible in the upper left section of figure 8. The line trace across the top of the picture is displayed in figure 9.

4. Discussion

Comparing the experimental and theoretical curves, all the results can in principle be accounted for by the one-dimensional model. However, the model depends on three

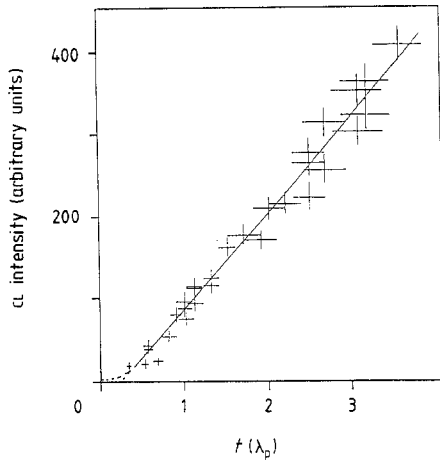


Figure 5. Thickness dependence of CL intensity observed in a type Ia diamond. The film thickness is expressed in terms of λ_p , the mean-free path for the valence electron excitation, which is about 68 nm.

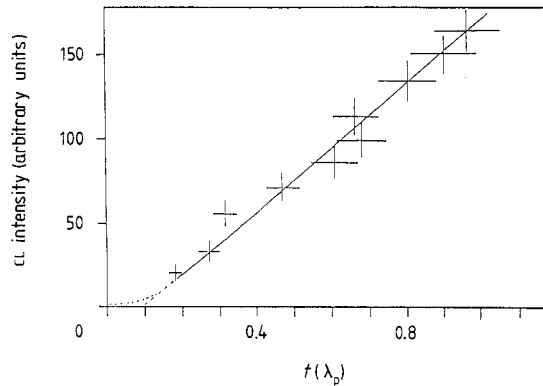


Figure 6. Thickness dependence of CL intensity observed in type IIa diamond. The film thickness is expressed in terms of, λ_p , the mean-free path for the valence electron excitation, which is about 68 nm.

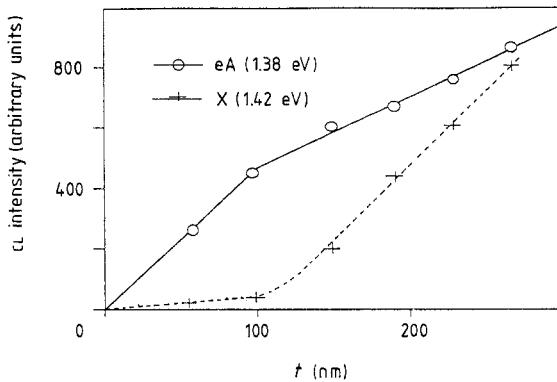


Figure 7. Thickness dependence of CL intensity observed in a semiconductor InP.

parameters of a thin film: its bulk diffusion coefficient D , its surface recombination velocity s , and the width of the possible surface dead layer t_d (which is luminescence-inactive). Only one quantity, the cut-off thickness, can be deduced from the thickness dependence of the CL intensities. This is not sufficient to determine three thin-film parameters. As stated above, the cut-off thickness is not even directly related to the crystal diffusion length. For YAG:Ce and InP crystals, the bending of the thickness dependence curves in the small thickness limit may allow us to estimate the ratio f in equation (11). When it is combined with the cut-off measurement, an estimate of the bulk diffusion length may then be deduced. Because of the paucity of the data and its limited accuracy due to noise, the bulk diffusion length deduced is not expected to be very accurate. A further complication arises from the existence of any possible surface non-luminescent layer. Table 1 summarises our data and those of Myhajlenko *et al* (1984).

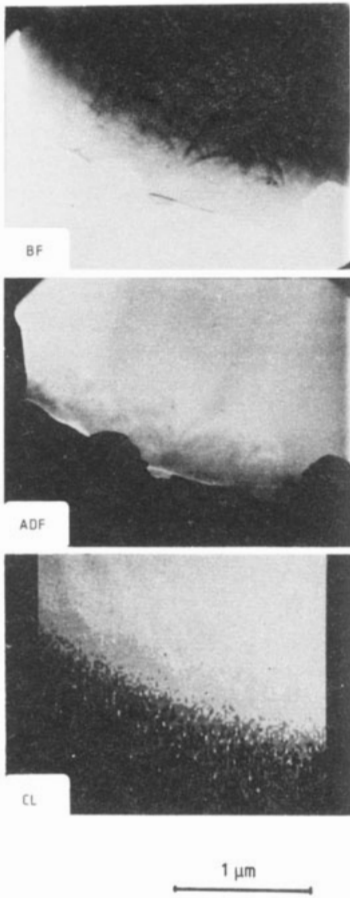


Figure 8. STEM bright field, ADF and CL pictures of a YAG:Ce crystal.

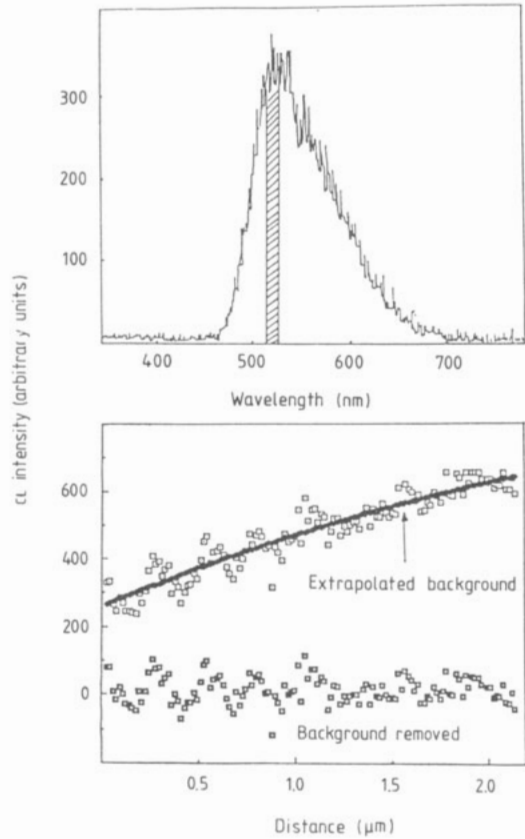


Figure 9. (Top panel) CL spectrum of a YAG:Ce³⁺ crystal, where the shaded band is the wavelength range of the light collected for CL imaging. (Lower panel) The line trace of the CL intensity across the top part of the CL image in figure 8, showing an intensity modulation on top of a smooth background.

Table 1. Summary of experimental results, where t_0 is the experimentally measured cut-off thickness, λ_p is the plasmon mean-free path used to estimate film thickness, and t_d is the experimentally observed CL surface dead layer thickness. Ia and IIa refer to two different types of diamond crystals, and X and cA refer to two types of luminescence from a single crystal of InP.

Sample	Y ₂ O ₃	YAG	Diamond		InP	
			Ia	IIa	X	cA
t_0 (nm)	32	60	10	20	200	~0
λ_p (nm)	210	80	68	68		
t_d (nm)	none	27				

4.1. Cut-off thickness and diffusion length in $Y_2O_3:Eu^{3+}$

As previously indicated, the experimentally determined cut-off distance depends on the diffusion length L and the surface dead layer thickness. In the case of a good phosphor like $Y_2O_3:Eu^{3+}$, the dead layer is expected to be very small. Exciton quenching can occur only if the excitons are within an orbital radius of the surface, which suggests a contribution to t_d of 1 nm or so. Because crystalline Y_2O_3 was prepared by grinding, no amorphous layer is expected, and none was observed. So the cut-off distance should truly represent a lower limit to the diffusion length of the electron-hole pairs. It is a lower limit because the surface recombination velocity may not be large.

The diffusion length will depend upon the concentration of recombination centres, for a typical lattice spacing d , defined as the Y-Y spacing, we may write

$$L = d(QC_{Eu^{3+}})^{-p/2}. \quad (15)$$

For $p = 1$, we have random hopping among metal ions. For $p = \frac{2}{3}$, we have a model in which the carrier wavefunction can sample activators in a 3D volume. Q is a numerical constant which depends upon the capture probability at each activator site. There is a variety of models which will produce different values of p and Q . At low concentrations (for $10^{-6} < C_{Eu^{3+}} < 10^{-4}$) Ozawa (1977) finds $Q \approx 1$ and $p \approx 2$. This yields a diffusion length of 9 nm for our material with $C_{Eu} = 0.04$. On the other hand, if the carriers are assumed to hop randomly from site to site, and to recombine at the first activator sites, $Q = 1$ and $p = 1$, from which we find a diffusion length of 2 nm. It seems most unlikely that such models can give rise to a diffusion length as long as 32 nm. It is worth noting that for lightly doped, luminescence-grade Y_2O_3 , the diffusion length can be as great as several microns (Ozawa 1977), but this is inappropriate for our materials.

For a thin film of $Y_2O_3:Eu$ crystal in STEM, typical beam currents in the probe are of the order of 10^{-10} A in a probe size of 1 nm diameter. The number of electrons passing through the sample is of the order of 6×10^8 s $^{-1}$. Assuming the film thickness to be 100 nm, then the number of electron-hole pairs produced is approximately $3 \times 6 \times 10^8$ s $^{-1}$ (assuming the electron-hole pair production rate is about 3×10^3 Å $^{-1}$ for fast electrons of 80 keV energy). The volume sampled by the electron-hole pairs is of the order of L^3 (assuming a three-dimensional random-walk model extending over a distance much larger than the probe size). Then, for an order-of-magnitude estimate, the Eu ions within that volume will be assumed to be all in excited states; that is, in the steady state, the number of the Eu ions within that volume is the number of excited Eu ions at any one time. The latter can be set equal to the product of the number of activators excited and the lifetime of the activator. The lifetime of the excited state is mainly determined by the spontaneous radiative transition rate from the 5D_0 state to the 7F_j manifold, which is about 900 μs (Buchanan *et al* 1968, Weber 1968). This gives an estimate of $L \approx 34$ nm. If a one-dimensional random-walk model is assumed, then the estimate would be even larger. The estimates can be reduced somewhat if one takes into account excited state relaxations (energy transfer among the activator subsystem to even out the distribution of the excited ions and cross-system quenching which reduces the number of excited ions). Nevertheless, the analysis shows that the most probable explanation of the observed cut-off is that the phosphor is highly excited by the electron beam, and most of the activators are in excited states when the diffusion occurs, so that most cannot act as recombination centres. The dependence of the CL spectrum on film thickness and on current density in the beam strongly suggests that saturation effects are important in the interpretation of these materials (Berger *et al* 1985).

As the lifetime of trivalent Eu ions is almost independent of the matrix, all Eu-doped material will show this enhancement effect. This also means that the spatial resolution of a CL image will depend to a certain extent on the excitation density. Therefore there is a limit on the extent to which one can improve the signal-to-noise ratio of the CL signal without losing the benefit of the small interaction volume in thin films.

4.2. *YAG:Ce*

The CL thickness variation curve also shows an almost linear relation between CL intensity and film thickness at large thickness values, but a smooth bending towards the origin at small thickness values, indicating that the surface recombination velocity in this crystal is not as large as, or comparable with D/L . The cut-off thickness observed in the thickness dependence curve of the thin-film luminescence can be accounted for by a combination of surface dead layer and bulk diffusion length. The surface dead layer due to the exciton effect will be small and unimportant. It is observed that in the thin-film region where the film is almost completely amorphous (due to ion-beam thinning), the CL intensity is only marginally different from that of the background and is almost constant over the complete amorphous region. Thus the amorphous layer is a dead layer as far as CL is concerned. The moderate surface velocity then refers to the interface between the amorphous layer and that of the YAG crystal. If one simply subtracts the thickness of the amorphous layer from the total film thickness, the remaining cut-off has the value of 15 nm and may be interpreted as twice the minimum size of the bulk diffusion length. The actual value of the electron-hole pair diffusion length could be much larger than 7.5 nm because of the finite surface recombination velocity (equation (11)).

A similar model can be used to estimate the excitation-dependent diffusion length in the YAG crystal. It is safe to assume that the electron-hole pair generation efficiency for fast electrons is about the same in order of magnitude as in $Y_2O_3:Eu^{3+}$. The important differences between the two crystals are the lifetimes of the excited states and the concentrations of the activator ions. The excited state of Ce^{3+} (which has only a single 4f electron in its ground state) is a 5d state, whose decay is electric-dipole-allowed and proceeds very quickly, with a lifetime of 70 ns (Owen *et al* 1981). Applying the same analysis as for Eu^{3+} , the result suggests a diffusion length of about 3 nm. Therefore, the excited states in $YAG:Ce^{3+}$ are not likely to be saturated under present experimental conditions.

However, the average distance separating the activators (about 0.9 nm), is a much smaller value than 7.5 (in a three-dimensional diffusion model). Either there is a thick layer not taken into account (for example, the surface dead layer may be thicker than the amorphous layer as the damage induced by ion-milling could extend further into the film), or the diffusion length is longer than expected because of the inefficient capture of electron-hole pairs by Ce^{3+} ions in the crystal. With respect to this latter possibility, it is noted that the absorption by this excited state has been observed to be large (Owen 1981) and the final absorption states are in the continuum above the band gap of the YAG crystal. Thus it appears that the trapped electron-hole pairs in addition to recombination may also be released from the activator and continue their interrupted random walk in the crystal, hence leading to a longer electron-hole diffusion length (i.e., $Q \ll 1$).

In general, no interference fringes are observed, perhaps because of surface roughness. The fringe system shown in figure 8 (CL) is an exception. A study of the variation of the separation of fringes as a function of the wavelength of the light selected through the monochromator was unfortunately not possible due to the loss of the sample during

analysis. However, the average CL intensity can give an estimate of the film thickness. For the thinnest part of the film where the fringes were observed the thickness is deduced to be about 200 nm. The film thickness difference between places, a fringe spacing apart, is about 80 nm. The refractive index at 500 nm is 1.84. Thus the difference in optical pathlength is about 150 nm, less than the half of the wavelength of the light (even when allowing for quite a larger error in the estimation of the foil thickness difference).

It is noted that silver dag has been used to fix the specimen on to the specimen grid. If the film is covered by the silver dag solution, the reflection will not only be enhanced, but will undergo a phase shift in π in each reflection. If the phase shift occurs at both sides of the film, the total phase shift is 2π and produces no net effect. If only one side of the film is covered, then a net phase shift in π is introduced. Thus the thickness difference between films a fringe spacing apart, need only be equal to a quarter of the wavelength divided by the refractive index. This agrees with experimental measurements, and is thus a strong possibility.

4.3. Diamond

In diamond, the blue band luminescence forms the most important contribution to the CL signals studied by the thickness-dependence measurement. It is known as band A, and is centred at 420 nm (Collins 1974). The luminescence is quite homogeneous on the submicrometre scale (Berger 1983), although inhomogeneity exists on macroscopic scales (Lang 1979). The luminescence band is thought to arise from the donor-acceptor recombination (Collins and Lightowers, 1979). Insulating diamond has an excess of deep-donor levels which in types Ia and IIa are thought to be due to nitrogen aggregates with an ionisation energy of 4 eV (Dean 1965). The most likely candidate for the acceptor is substitutional boron with an ionisation energy of 0.3 eV (Dean 1965). Type IIa diamonds have much less nitrogen impurity than Ia diamonds.

Because of the excess donor population, the acceptor is believed to be fully compensated. The binding energy of the donor levels is so deep that the electrons from the remaining uncompensated donors are not expected to contribute to the electrical conduction. This is consistent with the excellent insulating properties of these two types of diamond. Because of the charged nature of the compensated donor-acceptor pairs, the electron-hole pairs generated by the electron beam will be quickly captured by the charged centres. If one ignores for the moment the significance of other traps, the diffusion length of the free exciton is determined mainly by the average separation of the nitrogen aggregates. The concentration of nitrogen in diamonds depends on its growth condition. For type Ia diamonds, a nitrogen concentration as high as 0.3% has been recorded (Sellschop 1979). Assuming a three-dimensional model, the corresponding mean-free path of the exciton is about 1 nm. If we use the average value for the nitrogen concentration in type Ia diamond, which is about 780 ppm (Sellschop 1979), then the exciton diffusion length is about 1.5 nm. For type IIa diamond, the average nitrogen concentration is about 20 ppm (Sellschop 1979), then the estimated diffusion length is about 7 nm. This is certainly an underestimate since single substitutional nitrogen is not observed in either type of diamond, i.e., most of the nitrogen is believed to be locked in aggregates.

Our estimate of the bulk diffusion length for electron-hole pairs is crude, but it should give us the order of the magnitude of the quantity under consideration. As one can see, our estimate is quite close to that for the type IIa diamond. The estimate for the type Ia diamond is a little on the lower side. One possibility is that the nitrogen is locked

into relatively large aggregates in this type of diamond and the possibility of a surface dead layer is not ruled out.

4.4. InP

The luminescence monitored by Myhajlenko *et al* (1984) for InP crystal shows peaks X and eA. The peak X is centred at 1.42 eV and is attributed to a mixture of donor-bound and free-exciton transitions; the peak eA, centred at 1.385 eV, is a mixture of donor-to-acceptor and free-to-bound acceptor transitions, with the associated LO phonon replicas. The data for the thickness variation in InP are not as good as those presented above because of the larger probe used. Thus it is not certain that the cut-off for eA is exactly zero. Nevertheless, the data are interesting in that the two luminescence centres have roughly the same slope, yet quite different cut-off thicknesses. According to our simple model, this is a sign that the surface velocity for electron-hole pairs is almost zero, a conclusion confirmed by other measurements as well (Casey and Buehler 1977). A surface dead layer is not present for the electron-hole pairs (within the experimental errors). The large cut-off thickness has been attributed to exciton ionisation induced by a surface electric field (Myhajlenko *et al* 1984). Thus the cut-off is associated with an exciton-specific surface dead layer. The surface recombination velocity is again very small. It is interesting to note that the slope for the eA luminescence in figure 7 changes at a thickness equal to the exciton dead layer. This suggests that the electron-hole pair from ionised excitons reinforce recombination at the eA centre. Because of small surface diffusion velocity, we can not get an estimate of the bulk diffusion length for the electron-hole pairs.

5. Summary

The thickness dependence of cathodoluminescence from a number of electron-transparent films was investigated. It was observed that qualitatively the intensity variation can be accounted for by a simple model of electron-hole pair diffusion in thin films. The diffusion length of the electron-hole pairs can be inferred from a comparison between the model and experimental results. In the two rare earth ion-doped phosphor crystals, the measured value is larger than the average separation of the activators in the materials. Two mechanisms are thought to be responsible for this. In the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor, the long lifetime of the excited state of Eu^{3+} prevents efficient binding of further electron-hole pairs, thus the effective concentration of the activators is reduced. In $\text{YAG}:\text{Ce}^{3+}$, the Ce^{3+} ion luminescence is a very rapid process. Thus the depletion of the activators in the ground state is not a serious problem, but one has to consider the possibility of excited state absorption, leading to less than 100% probability of electron-hole pair binding. In the two types of diamond, the diffusion length deduced is very approximately the same as that expected from the nitrogen impurity concentration. The situation is slightly complicated by uncertainty about the existence of a non-luminescent surface layer of graphite. This simple model is also applicable to semiconductors. In InP, the analysis confirms that the surface velocity of that material is very small and there exists an exciton dead layer about 60 nm wide. Because very little information can be extracted from the CL experiments from thin films, most of such explanations suggested so far are only tentative, and need to be discussed in consideration with other experimental evidence. Nevertheless, the principle behind the model is quite general, and the model

offers a simple means to characterise the behaviour of the thickness dependence of the luminescence from specimens in the transmission electron microscope.

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