Spatially resolved cathodoluminescence of luminescent materials using an EDX detector

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Summary
Panchromatic cathodoluminescence (CL) maps were collected in a scanning electron microscope equipped with an EDX (energy dispersive x-ray analysis) detector. These CL maps can readily be correlated with elemental maps obtained by EDX. Although EDX detectors are designed to be insensitive to light and therefore not optimized for high sensitivity CL measurements, high-resolution images can be obtained from luminescent materials without the need for additional hard- or software. The method was tested on highly luminescent BaAl_2S_4:Eu^{2+} thin films that have a potential use in flat panel displays. The spectral response and linearity of the overall system was determined by means of monochromatic light sources, illuminating the sample through an optical fibre. We studied the response of the EDX detector to the intensity of the incoming light as well as the influence of the detector settings. The observations were explained by numerical simulations.

Introduction
Cathodoluminescence (CL) detection with a scanning electron microscope (SEM) is a powerful technique for investigating the lateral distribution of defects in semi-conductors and insulators (Yacobi & Holt, 1986; Poelman et al., 2001; Poelman et al., 2004; Hidalgo et al., 2005; Martinez et al., 2007) as well as in mineralogy (Townsend et al., 1999; Edwards et al., 2007; Pownceby et al., 2007). Depending on the energy of the primary beam (Petrov, 1992; Donolato, 1994; Gelhausen et al., 2001), the technique couples a sub-micron spatial resolution (Gustafsson, 2006), to an excellent detection limit (Yacobi & Holt, 1986) that is orders of magnitude better than what is achievable with other techniques for micro-analysis, like Auger electron spectroscopy (AES) and EDX. One of the strengths of CL is that it can easily be combined with other analytical techniques, such as EDX (for elemental analysis) and EBSD (for micro-structural analysis) (Macrae et al., 2005; Piazolo et al., 2005).

SEM-CL is not widely used as an analytical tool, partly because its virtues are not well known but also because the investment needed to mount a complete CL attachment (including monochromatic imaging) to an SEM (or a TEM) is considerable. If only the intensity of the generated light is needed, it is also possible to use a rudimentary CL system. In any case, mapping the CL over the surface of the specimen requires communication between the light detection system and the scan generator of the electron microscope. In the present paper, we report on the use of an EDX detector, which is available as a standard extension to a large number of electron microscopes, for the detection of CL. Light entering the EDX detector creates a spurious signal in the low energy part of the EDX spectrum, which can readily be used to map the CL emission. This map can then be correlated to elemental maps that were simultaneously acquired. Because the EDX detector integrates over the entire visible wavelength range, the obtained CL maps are panchromatic (Strunk et al., 2006). In this work, we will illustrate how to exploit this feature and demonstrate how this ‘artefact’ arises from the EDX detection system.

Materials and methods
Measurements were performed using a FEI Quanta 200 SEM, equipped with a heated field emission gun, allowing for a beam size down to a few nm. Attached to the SEM was an EDAX Genesys 4000 with a Sapphire Si(Li) detector. This type of detector has a super ultra thin window (SUTW), which consists of a 0.3-μm polymer foil coated with DuraCoat™, a

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proprietary refractive coating material that contains elements lighter than sodium only. To minimize the amount of light entering the EDX detector, the window has an additional 40-nm Al-coating. The window is supported by a silicon grid with 77% open area. The effective window area of the detector is 10 mm$^2$, resulting in an overall transmission that is very high for low-energy x-rays (for instance, 47% for the C K$\alpha$ line). Figure 1 shows the window transmittance for visible light. The transmission is very low, so one would expect the light sensitivity of the detector to be negligible.

The linearity and wavelength-sensitivity of the EDX detector (including the SUT/W) were tested by illuminating the sample area of the SEM with visible light. Light from several high-efficiency red, green and blue LEDs was fed into the SEM vacuum chamber via an optical fibre. All LED spectra and brightness/current characteristics were measured separately by means of an FS920 emission spectrometer (Edinburgh Instruments, Reading, UK) and a calibrated J1812 photometer (Tektronix, Bracknell, UK), respectively. To verify the correctness of the CL maps that were collected with the EDX detector, a specific set-up was built to obtain CL images in a more conventional way. The CL light was then coupled to an optical fibre that was pointed at the e-beam irradiated sample and detected by means of a QE 65000 CCD spectrometer (Ocean Optics, Dunedin, FL, USA). CL maps were obtained from these optical spectra with the help of software specifically written to this end. Finally, these maps were related to the correctness of the CL maps that were collected with the EDX detector, the window has an additional 40-nm Al-coating. The window is supported by a silicon grid with 77% open area. The effective window area of the detector is 10 mm$^2$, resulting in an overall transmission that is very high for low-energy x-rays (for instance, 47% for the C K$\alpha$ line). Figure 1 shows the window transmittance for visible light. The transmission is very low, so one would expect the light sensitivity of the detector to be negligible.

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As an example, the CL of BaAl$_2$S$_4$:Eu thin films was studied. This blue-emitting, electroluminescent material is very promising for the realization of full colour flat panel displays (Miura et al., 1999; Miura et al., 2000; Guo et al., 2006). Thin films with a thickness of about 1 μm were prepared by electron beam evaporation of a multi-layered BaS:Eu/Al$_2$S$_3$ structure. A post-deposition annealing in oxygen (800°C, 60 s) yielded BaAl$_2$S$_4$:Eu thin films through solid state reaction of the individual layers. More details on the sample preparation can be found elsewhere (Smet et al., 2004; Smet et al., 2005a,b). The following characteristic x-rays were monitored for the elemental maps: Al K (1.49 keV), O K (0.53 keV), S K (2.31 keV), Si K (1.74 keV) and Ba L (4.46 keV). The CL signal was mapped by defining a region of interest (ROI) for the energy channels between 0 and 180 eV. The photoluminescence of the BaAl$_2$S$_4$:Eu thin films was measured separately with a FS920 fluorescence spectrometer (Edinburgh Instruments) at an excitation wavelength of 350 nm.

Results and discussion

Why is an EDX detector sensitive to (visible) light?

To fully understand how an EDX detector and its signal processor interpret incoming light, one has to look into the details of the EDX detection system (Fig. 2). When a high-energy photon (an x-ray) strikes the Si(Li) detector, it generates – almost simultaneously – a number of electron-hole pairs, proportional to the energy of the incoming photon. This charge is collected by applying a voltage over the detector and converted to a voltage by a pre-amplifier. To avoid saturation of the pre-amplifier, the charge is periodically restored. The resulting signal to be analyzed, is a stepwise increasing voltage (each step corresponding to an incoming x-ray, Fig. 2(2)) and an abrupt step down (Fig. 2(7)). Detector leakage adds a small ramp to this profile. By using ‘strobing’, which is the monitoring of the baseline if no x-ray events are detected, the analysis software corrects for the detector leakage so that no peak shifts are induced by this small ramp (Fig. 2(5)).

The purpose of the pulse processor and software is to determine the height of the upward steps as accurately as possible. As this signal contains noise, the accuracy of the determination of the x-ray energy can be improved by averaging the signal during several micro-seconds (between 3.2 and 102 μs for the set-up used) before and after an x-ray event (Fig. 2(1) and (3)). The accuracy and resolution are improved with increasing averaging time, but this comes at the cost of throughput. If the count rate is high, there is – on average – too little time between events to average the signal. If a signal step (corresponding to an incoming x-ray) occurs during averaging, this particular measurement has to be discarded (Fig. 2(6)), leading to an increase of the detector dead time. This means that when measuring a moderate to high rate of incoming x-rays, the effective count rate decreases with increasing averaging time.

If light enters the detector, the type of signal is completely different. A visible light photon, with a typical energy between 2eV (wavelength 620 nm, red light) and 3eV (wavelength...
For the sake of simplicity, let us consider what happens when only light and no x-rays are forming the signal. First, the voltage signal is averaged during a pre-set time (3.2–102 μs). The signal is then continuously monitored, and the instrument decides that a new event (normally this is an incoming x-ray) has taken place when the voltage has increased from this average to a certain threshold. This threshold is set in the calibration of the system (i.e. the BLM or ‘base line monitor’ value in the EDAX software) and is chosen to be dependent on the averaging time. The uncertainty on the averaged voltage level decreases for increasing averaging time, which implies that lower x-ray energies can be detected when using longer averaging times. The BLM value is therefore generally set higher for shorter integration time so as to avoid the generation of low-energy peaks by the noise on the voltage signal. As discussed earlier, light entering the EDX detector creates a voltage ramp, of which the steepness is directly related to the intensity of the incoming light. The higher this intensity, the faster a new ‘event’ is triggered upon exceeding the BLM threshold value. This artificial creation of x-ray events is enhanced when longer averaging times are used because of the lower threshold value and the longer accumulation time for the light-generated voltage contribution.

An example: BaAl$_2$S$_4$:Eu thin films

As an example, luminescent BaAl$_2$S$_4$:Eu thin films were studied in the SEM-EDX system. BaAl$_2$S$_4$:Eu is a blue-emitting...
material with a single-emission band centred at 470–475 nm due to a transition from the 4f\(^6\) 5d to the 4f\(^7\) state in Eu\(^{2+}\). This transition can be efficiently excited both by UV light and by an electron beam, yielding identical emission spectra (Fig. 3). An important issue in the development of this material for use in electroluminescent flat panel displays is its stability against hydrolysis. Contact with moisture leads to a degradation of the layers with the development of hydrogen sulphide, the (gradual) loss of the luminescence and an amorphization of the thin films. Figure 4 shows the result of elemental maps on a BaAl\(_2\)S\(_4\):Eu thin film that was exposed to ambient air during several hours. In comparison with the freshly prepared sample, the photoluminescence (PL) intensity had already partly decreased. The cracks in the thin film (black lines in the SEM image) are reflected in the EDX mapping on Si. In these cracks, it is possible to obtain the characteristic x-ray lines for Si originating from the silicon substrate. The CL mapping, obtained by integrating the intensity in the EDX spectrum for the energy channels up to 180 eV, clearly shows an inhomogeneous distribution of the CL. Correlating this CL signal to the elemental x-rays for oxygen and sulphur, we observe that a lower CL signal corresponds to an increased oxygen content in combination with a reduced sulphur signal. This is clearly related to the degradation, that is the hydrolysis, of the BaAl\(_2\)S\(_4\):Eu thin film.

The PL shows a gradual decrease in intensity with increasing exposure to ambient air (not shown), whereas the PL spectrum (measured separately outside the SEM) remains unchanged. However, based on the CL maps, one clearly sees that the degradation occurs inhomogeneously with entire ‘grains’ [i.e. the micron-sized regions in between the large, annealing-induced cracks (Fig. 4)] still emitting, whereas other ‘grains’ are already degraded. The specific degradation behaviour of the BaAl\(_2\)S\(_4\):Eu thin films annealed in oxygen is the subject of ongoing research, although it is speculated that the annealing in oxygen leads to a protective oxide layer on top of the thin film. The thin film starts to degrade once this protection is broken. Small cracks are formed, through which moisture further penetrates into the BaAl\(_2\)S\(_4\):Eu layer, causing hydrolysis and leading to further degradation. On the right side of the mapped area in Fig. 4, a (rare) partially degraded area is visible.

To evaluate the correctness of this method (mapping the CL with the EDX detector) (Fig. 5(A)), the same area as in Fig. 4 was mapped by leading the generated light to a CCD spectrometer through an optical fibre (Fig. 5(C)). Clearly, there is a good quantitative correspondence between both images, showing the strongly luminescent grains in contrast to the dark areas. It is interesting to note that most of the grain edges have a higher CL emission for both

![Secondary electron image (centre) of a partly degraded BaAl\(_2\)S\(_4\):Eu thin film, along with elemental maps on barium, aluminium, sulphur, oxygen and silicon. The ‘CL’ mapping was obtained by integrating the intensity in the EDX spectrum for the energy channels up to 180 eV.](image-url)
Fig. 5. (A) CL mapping on a slightly reduced area compared with the one shown in Fig. 4, obtained by integrating the intensity in the EDX spectrum for the energy channels up to 180 eV. (B) CL mapping obtained by re-scaling the logarithm of the intensities as shown in (A). (C) CL mapping obtained by detecting the emitted light with a CCD spectrometer. The arrows indicate the grain edges where both detection methods show an increased emission intensity.

mapping methods (indicated by the arrows in Fig. 5). In section The Response of the EDX Detector to (Visible) Light, we will show that the response of the EDX detector relates exponentially to the light intensity, in contrast to the linear response of the CCD spectrometer. Therefore, we calculated Fig. 5(B) as the logarithm of the intensities measured with the EDX detector (Fig. 5(A)) and we now obtain a quantitative correspondence with the ‘normal’ CL image detected with the CCD spectrometer.

Based on the mappings shown in Fig. 5, the spatial resolution appears the same for both detection systems. In the example shown here, one is not working close to the possibly obtainable resolution with SEM-CL (Norman, 2000). Nevertheless, the way of detecting the CL emission with the EDX detector can be expected to have the same spatial resolution in comparison with a ‘standard’ SEM-CL detection system, as there is no physical difference in the excitation mechanism.

The response of the EDX detector to (visible) light

To get an idea of the sensitivity of the EDX detector for use as a CL probe, we deliberately coupled light into the SEM sample chamber through an optical fibre. To eliminate geometry effects, this light was shone onto a strongly light-scattering piece of white PTFE. By using the standard settings of the EDX software, the number of light-generated counts in the low-energy part of the spectrum was then evaluated as a function of the intensity of the incoming light and the integration time (Fig. 6).

Three effects were observed from Fig. 6. First, for each integration time, there is a threshold below which light does not generate intensity in the low-energy part of the EDX spectrum. Second, the sensitivity of the EDX system strongly depends on the value of the integration time; the longer the integration time, the more sensitive the system becomes. This observation is in line with the analysis made in section Why Is an EDX Detector Sensitive to (Visible) Light? and will be further explored in section Simulating the Detector Behaviour. Finally, the count rate depends almost exponentially on the light intensity. Correcting mappings for this dependence therefore gives a good correspondence with the ‘normal’ way of CL detection (Fig. 5).

The next step was the evaluation of the wavelength dependency of the EDX detector, which was performed by using different LEDs with relatively small spectral band widths. It appears that the response of the EDX detector to light is quite wavelength-dependent, being highest for green light ($\lambda = 520$ nm), lower for blue ($\lambda = 470$ nm) and lowest for red ($\lambda = 630$ nm). This dependency results from the two main components in the EDX detector, namely, the detector window and the Si diode itself. In Fig. 1, one can see that the optical transmission of the detector window is highest for green light,
and lower for blue and red. The Si diode sensitivity is most probably lower for near-UV to deep-blue photons, due to the shorter absorption length in Si. On the long wavelength side (near-IR), the light detection is limited by the fundamental band edge of Si (at about 1.1 eV or 1100 nm).

Simulating the detector behaviour

To explain the experimental results of Fig. 6, numerical simulations were performed using Matlab™. A program was written to simulate the electrical response of the EDX detector, initially without the input of (visible) light. The following features were included (1) the presence of a (small) detector leakage, (2) a Gaussian-distributed noise superposed on the detector signal, (3) a variable detection limit, corresponding to the minimum energy of an event (similar to the parameter BLM mentioned earlier), (4) a variable integration time, (5) the random generation of x-ray events (arbitrarily taken at 2 keV), (6) binning and output of the obtained events in 10 eV-wide energy channels, (7) calculation of dead time and count rate. The program was written according to the procedure shown in Fig. 2.

The validity of the program was first tested by simulating the EDX behaviour in ‘normal’ mode, that is without the additional input of visible light. Because of the noise on the detector signal, the (monochromatic) x-rays get a certain width in the simulated spectrum (Fig. 7(a)). Increasing the integration time reduces the full width half maximum of the x-ray peaks, in line with the experiment (not shown). In case of a high rate of incoming x-rays, the dead time increases when using a longer averaging time. Because this is in line with the experimental observations, the Matlab™ program simulates the EDX detector behaviour correctly.

We then simulated the effect of (visible) photons falling on the detector. Given the low photon energy (<3 eV), the incoming light was considered a continuous signal. As mentioned previously, the steepness of the ramp superposed on the EDX signal can be considered to be proportional to the intensity of the incoming light. Figures 7(b) and (c) show simulated EDX spectra when visible light falls onto the detector. Apart from the ‘normal’ x-ray events at 2 keV a second signal arises on the low energy side. Figure 8 shows the response (i.e. the count rate in the low energy part of the spectrum) as a function of the incoming light intensity and the integration time. A non-linear response curve is obtained irrespective of integration time, which corresponds with the experimental observation (Fig. 6). Furthermore, increasing the integration time strongly increases the light sensitivity (Fig. 8) as well as the dead time (not shown), again in line with the experiment. The increase in dead time is reflected in the smaller dynamic range for high integration times (Fig. 8). During the simulation of the integration time, the event detection limit (i.e. the value for BLM) was kept constant. As mentioned before, the value of BLM in the EDX software is generally set lower for longer integration times. The light sensitivity at long integration times then further increases upon decreasing the BLM value (not shown) because of the lower threshold. Based on experiment and simulation, the light sensitivity of the EDX detection system is strongly influenced by both effects (i.e. integration time and BLM value).

It was experimentally verified that detection of visible light by the EDX detector does not strongly influence the peak

Fig. 7. Simulated EDX spectra with random x-ray events at 2.0 keV, as a function of the visible light intensity. The dead time (DT) is shown as well. For better visibility, the spectra were displaced with respect to each other.

Fig. 8. The simulated count rate in the low-energy part of the EDX spectrum induced by the input of visible light as a function of light intensity and integration constant value: (a): 2, (b): 5, (c): 11.
positions of the ‘normal’ x-ray peaks, provided that the dead time stays within reasonable limits (<80%). This proves that the monitoring of the baseline (strobing) is successfully applied. This is also the case in the simulation program, as no peak shifts are observed (Fig. 7). For very high count rates, the detector saturates and peak shifts are observed along with significant peak broadening.

Conclusions

In this work, we have shown that it is possible to use an EDX detector as a probe for the CL in an electron microscope. Under specific conditions, CL emission generates a spurious signal in the low part of the EDX spectrum (<200 eV), which can effectively be used to obtain panchromatic CL maps. The EDX detector is sensitive to the entire visible spectrum, although the response is not flat due to wavelength-dependent absorptions in the detector window and the Si diode. We have explained how this signal arises by combining experiments in the SEM with numerical simulations. The validity of the method was proven by comparing the results with maps obtained with a conventional CL set-up (using a CCD). Both CL mapping methods are in good correspondence.

The small acceptance angle of the EDX detector, the deliberately low sensitivity for visible light (due to the metal-coated window) and the lack of spectral resolution imply that the present set-up cannot compete in sensitivity or in flexibility with a commercial SEM-CL attachment. As such, it is only useful for studying materials with a good CL efficiency. Since the CL maps can be combined simultaneously with secondary electron imaging and elemental mapping using EDX, a wealth of information is available from a single measurement, simply by defining an appropriate region of interest (ROI) and carefully choosing the detector settings. As an example we have illustrated its use for the study of the degradation in BaAl$_2$S$_4$:Eu thin films. As an EDX extension is attached to most electron microscopes, one has easy access to panchromatic CL mapping, even in a transmission electron microscope (Strunk et al., 2006) where a dedicated CL system is not so common.

For users who are not interested in the CL of their samples, the presence of CL can distort the recording of EDX spectra. Apart from the observation of an additional peak at low energy, a strong light signal increases the dead time of the detector. At even higher light intensities, the characteristic x-rays can show an energy shift, leading to erroneous elemental analysis results. As a general guideline, the influence of (visible) light on the x-ray signals in the EDX detector can be minimized in two ways by reducing the CL signal or by changing the detector settings. On the one hand, the CL signal detected by integrating the low-energy signal in the EDX spectrum is highly non-linear with respect to the intensity of the electron beam, whereas the x-ray signal is generally not. This means that reducing the spot size (and correspondingly reducing the current of the exciting electron beam) can suppress the CL signal generated in the EDX spectrum, while only moderately reducing the x-ray signal. Alternatively, the deposition of a thin metallic layer on the sample surface (Au, for instance) will cause considerably absorption of the generated CL, whereas the x-rays generated in the sample are mostly transmitted.

By contrast, one can also change the detector settings to reduce the CL signal. Decreasing the integration time lowers the sensitivity to the (visible) light. The downside to this method is that the width of the ‘normal’ x-ray peaks increases simultaneously, which can lead to peak overlaps. Another remedy is to increase the threshold level (the BLM value) for the detection of an x-ray event. Although this will compromise the detection of low-energy x-rays (B, C, N,…), it is an efficient way to eliminate the light-generated low-energy peak while keeping resolution and sensitivity for most characteristic x-rays.

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