Cathodoluminescence hyperspectral imaging on the nanometre scale

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***Abstract*—Extending cathodoluminescence microscopy into the hyperspectral imaging mode brings significant benefits to an already powerful nano-scale characterization tool. In this paper, we give an introduction to the technique, and illustrate its potential with examples of its application to both semiconducting and plasmonic nanostructures.**

Keywords-hyperspectral; cathodoluminescence; microscopy; spectroscopy; SEM; semiconductor

I. INTRODUCTION

Cathodoluminescence (CL) is the phenomenon of light emission from a material under stimulation by a beam of energetic electrons. Spectroscopy and microscopy of this luminescence is well established as an analysis technique in a number of fields, including optoelectronic semiconductor research and the geosciences. With a resolution dependent only on the spatial distribution of charge carriers generated by the beam/sample interaction, CL has the advantage over other luminescence techniques in not being subject to the optical diffraction limit. The extension of CL to the hyperspectral imaging (HSI) mode [1-2] has made the technique more powerful still, allowing the mapping of subtle shifts in luminescence characteristics such as peak wavelengths and widths that was previously not possible using spot-mode spectroscopy or monochromatic imaging. We will introduce the technique, examine technical aspects of the measurement such as design considerations for efficient collection optics, and discuss the applicability of multivariate statistical analysis to the results. We illustrate these points with examples from our own experience of designing and constructing CL systems and applying the technique to the characterization of a range of semiconducting materials and nanostructures.

II. MEASUREMENT

Cathodoluminescence is most commonly measured using an adapted scanning electron microscope (SEM), in which an electron beam is focused to the sample surface and the resultant emitted light collected for analysis. Conventional CL measurements have then been carried out in one of two modes. In monochromatic imaging mode, the emission intensity of a given wavelength band is recorded as the beam is scanned in a raster pattern across the sample; this can be used for example to map areas of high carrier recombination such as crystal dislocations and grain boundaries. In the second approach, a spectrum of the emission is acquired at a fixed beam position, giving an insight into, for example: composition, elastic strain, impurities and defect densities. In CL hyperspectral imaging, a full spectrum of the emitted light is recorded at *each pixel* during the scan, building up the multidimensional dataset one spectrum at a time. Figure 1 shows a schematic of such a system based on a high-resolution field-emission SEM [3]. With the sample tilted, a reflecting objective collects the emitted light which is focused using an off-axis parabolic mirror to an f/number-matched image at the entrance slit of a CCD spectrograph. This all-reflecting optical design eliminates chromatic aberration and also allows wavelengths down to 200 nm to be measured from UV-emitting materials such as aluminium nitride and diamond. Using this system we have probed CL variations on length scales approaching 10 nm [4].

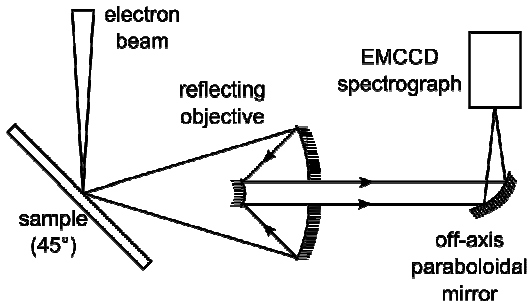

Figure 1. Schematic of a high resolution SEM CL system

III. SEMICONDUCTOR NANOSTRUCTURES

Figure 2 shows an example of using CL HSI to measure an array of nano-scale gallium nitride (GaN) pyramids [5]. The features were formed by metal-organic chemical vapour deposition thought a silica mask into which an array of holes had been patterned, with the wurtzite crystal structure of the material resulting in hexagonal-based nano-pyramids. This is shown in the secondary electron SEM image in Figure 2(a).

Such structures offer a method of growing low dislocation density material for optoelectronic applications such as LEDs [5], as well as having potential application as single photon emitters due to the formation of quantum dots [6]. The pyramids contain a highly-luminescent quantum well of the alloy $In_xGa_{1-x}N$, giving excitonic emission at ~3.0 eV, with additional peaks from the underlying GaN at 3.4 and 2.2 eV. By non-linear least squares fitting of multiple Gaussian peaks to each spectrum, and plotting out the resultant fit parameters as an image, the spatial variation of various aspects of the emission can be plotted. Figure 2(b) shows, for example, the fitted peak energy of the QW emission.

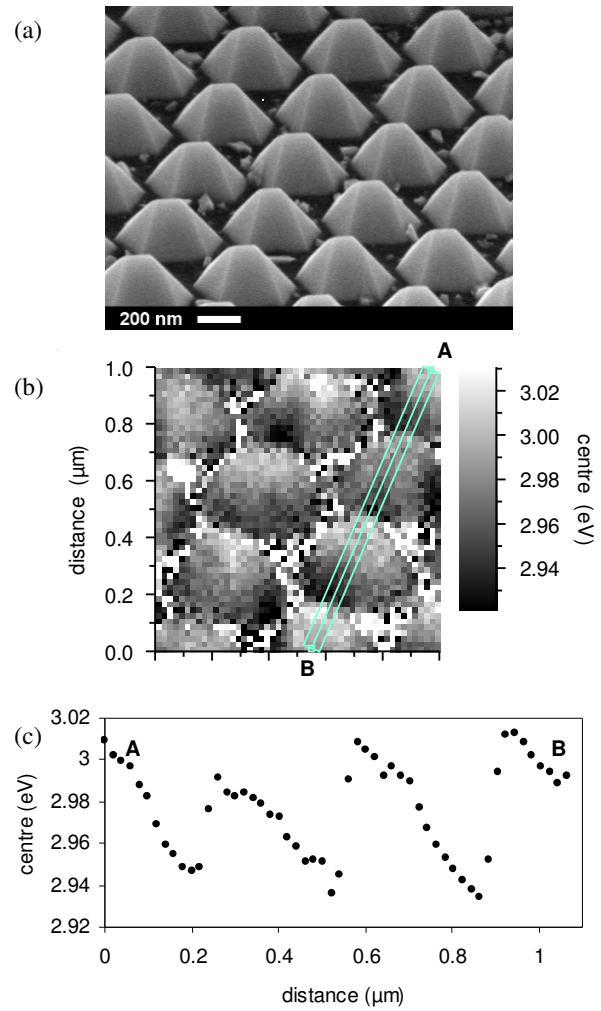

Figure 2. (a) SEM image of GaN nanopyramids and (b) map of peak CL energy, derived by peak fitting to the HSI.

This shows the emission wavelength varying with distance from the pyramid apex, behaviour demonstrated more clearly in the associated linescan in Figure 2(c). This is interpreted as being due to a reduction in the InN fraction within the $In_xGa_{1-x}N$ QW in the regions closer to the apex. The generation of this type of CL image would not be possible without the use of the hyperspectral imaging mode.

IV. Plasmonic Nanostructures

Another, entirely different, mechanism by which electron beams can induce light emission in nanostructures is through the coupling of the beam energy into localized surface plasmon modes [7]. The resultant emission is typically much lower in intensity than that due electron-hole recombination in semiconducting materials, and presents a challenge to current instrumentation. An example of using CL HSI to investigate such nanostructures is shown in Figure 3.

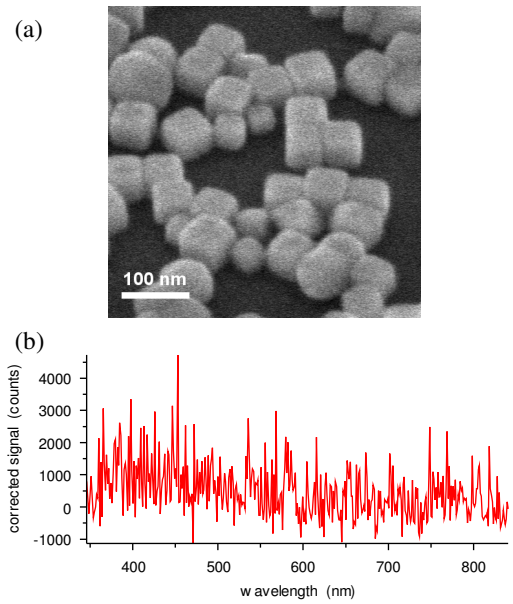

Figure 3. (a) SEM image of silver nanocubes on silicon substrate, and (b) a typically noisy measured CL spectrum from the cubes.

This sample consists of ~50 nm silver cubes on a silicon substrate, as seen in the SEM image in Figure 3(a). The observed luminescence results from the decay of the induced plasmon resonances [8], and is of an intensity barely above the detection threshold of the CL system. This can be seen in a typical spectrum in Figure 3(b), which shows the very low signal:noise ratio. However, the application of principal component analysis (PCA) to the data allows distinct spectral features to be isolated within the noisy signal. This was carried out by finding the eigenvectors of the $n \times n$ covariance matrix formed from all of the n-channel spectra in the dataset, and performing a *varimax* orthogonal rotation on the first three components. The results of this analysis are shown in Figure 4. Comparison with the results of numerical simulations has allowed these peaks to be identified as corresponding to different plasmonic modes [9]. By using these spectra as basis functions for extracting images from the HSI, the spatial distribution of these modes has been plotted. The shortest wavelength peak was found to be localized at the edges and corners of the cubes (Figure 4 top left), for the first time allowing confirmation of theoretical predictions in features of this scale.

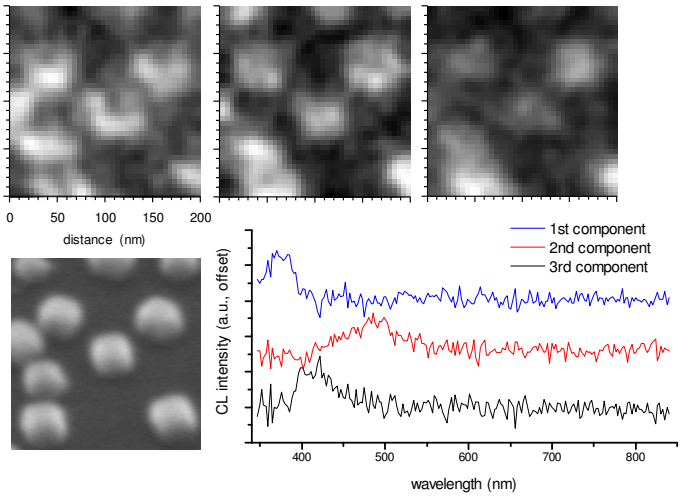

Figure 4. (Top, left to right) First three principal components (PCs) of CL from Ag cubes. (Bottom) Secondary electron SEM image of the same area and spectra for the first three PCs

V. Combined Datasets

One of the significant strengths of the scanning electron microscope is the ability to measure different signals induced by the beam-sample interaction *simultaneously*. These include, for example, secondary and backscattered electrons and X-rays, in addition to cathodoluminescence. This makes it possible to carry out different measurements concurrently, and directly correlate different microscopic properties of the material without the alignment errors associated with *ex-situ* measurements.

As an example of this multimode SEM functionality, we have developed another CL hyperspectral imaging system based on an electron probe microanalyzer. This system allows the wavelength dispersive spectroscopy (WDS) of characteristic X-rays which are generated by the electron beam in the sample, allowing quantitative mapping of the atomic composition of the material. Simultaneously measuring the CL allows the direct correlation of emission and composition properties on a sub-micron scale; this is particularly important in the study of alloy semiconductors in which microscopic fluctuations in composition can play a crucial role in determining the luminescence properties [2].

The acquisition of such combined CL/X-ray fluorescence datasets has also been useful in the study of geological materials, in which CL can be used as a proxy to detect the presence of elements at trace levels undetectable through WDS alone [10]. We have then used PCA of these combined CL/X-ray datasets in order to identify statistical correlations between the intensity of spectral features and the abundance of particular elements [11].

VI. Conclusions

Extending the technique of cathodoluminescence to the hyperspectral imaging mode offers a number of specific advantages over the more established variants on monochromatic imaging and spot-mode spectroscopy. These include: the facility to map spectral shifts in emission peaks; the identification of small signals within large noisy datasets; and the exploitation of the multidimensional nature of the datasets using multivariate statistical analysis methods. For further details of the examples outlined in this paper, the reader to referred to [3-5, 8].

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