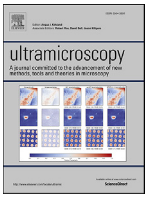
Ultramicroscopy 000 (2017) 1–20

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic



Cathodoluminescence in the scanning transmission electron microscope

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ARTICLE INFO

Article history:
Received 29 July 2016
Revised 16 November 2016
Accepted 18 November 2016
Available online xxx

Keywords:
Cathodoluminescence
STEM
Nano-optics
Plasmonics
Quantum emitters
Band gap measurements

ABSTRACT

Cathodoluminescence (CL) is a powerful tool for the investigation of optical properties of materials. In recent years, its combination with scanning transmission electron microscopy (STEM) has demonstrated great success in unveiling new physics in the field of plasmonics and quantum emitters. Most of these results were not imaginable even twenty years ago, due to conceptual and technical limitations. The purpose of this review is to present the recent advances that broke these limitations, and the new possibilities offered by the modern STEM-CL technique. We first introduce the different STEM-CL operating modes and the technical specificities in STEM-CL instrumentation. Two main classes of optical excitations, namely the coherent one (typically plasmons) and the incoherent one (typically light emission from quantum emitters) are investigated with STEM-CL. For these two main classes, we describe both the physics of light production under electron beam irradiation and the physical basis for interpreting STEM-CL experiments. We then compare STEM-CL with its better known sister techniques: scanning electron microscope CL, photoluminescence, and electron energy-loss spectroscopy. We finish by comprehensively reviewing recent STEM-CL applications.

1. Introduction

Cathodoluminescence (CL) i. e. the emission of light from a material upon interaction with an electron, is a well-known phenomenon. As a regular characterisation technique, it has been applied with great success in geological sciences and for the characterisation of semiconductors [1]. In the past fifteen years it has undergone a major rebirth related to the development of optically active nanomaterials and nanostructured materials. This rebirth is certainly linked to the fact that an electron beam can be made arbitrarily small compared to the nanometer scale at which the three main phenomena that are driving the optical behaviours of nanomaterials or nanostructured materials occur. In other words, such phenomena happen at scales that are hardly reachable with conventional far-field diffraction limited optical techniques. In contrast, modern Scanning Electron Microscope (SEM) or scanning transmission electron microscopes (STEM) can nowadays form extremely small electron probes (< 1 nm) and benefit from optimised light detection schemes. Although such small probes can lead to very small excitation volumes, they do not lead necessarily to high spatial resolutions. However, we will see that under certain circumstances they do, which justifies in part the writing of this review.

The three main phenomena under discussion (see Fig. 1) are:

- *Plasmon confinement* (Fig. 1a): standing waves made up of a mixture of charge density waves and photons form at the surface of nanoparticles when their sizes become comparable to the wavelength of light [2]. These are surface plasmons (SPs). Their resonance frequency depends on the size and geometry of the nanoparticles, and can thus be tuned by changing these parameters; it also depends on the local dielectric environment of the nanoparticle. Because they are resonant, these excitations dominate the optical spectrum of small metallic nanoparticles. Finally, SPs make it possible to concentrate the electromagnetic field at the nanometer scale. These properties - size and shape resonance-energy dependance, local environment sensitivity, electromagnetic energy focusing - indicate a bright future for SP applications such as sensing or cancer therapy.
- *Band gap variations at the nanometer scale* (Fig. 1b): the energy band-gap in a semiconductor largely determines its absorption properties, and, if it is luminescent, its luminescence properties. In semiconductors or insulators, luminescence arises through the creation of charged carriers (electron-hole pairs in case of CL or photoluminescence, PL) that subsequently recombine radiatively. In the absence of deep recombination centres (see later), most of the recombinations arise close to the band gap energy. Minor differences between the emitted light and the band gap energies may be due to the presence of shallow defects close to the valence or conduction band to/from which

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http://dx.doi.org/10.1016/j.ultramic.2017.03.014

Please cite this article as: M. Kociak, L.F. Zagonel, Cathodoluminescence in the scanning transmission electron microscope, Ultramicroscopy (2017), http://dx.doi.org/10.1016/j.ultramic.2017.03.014

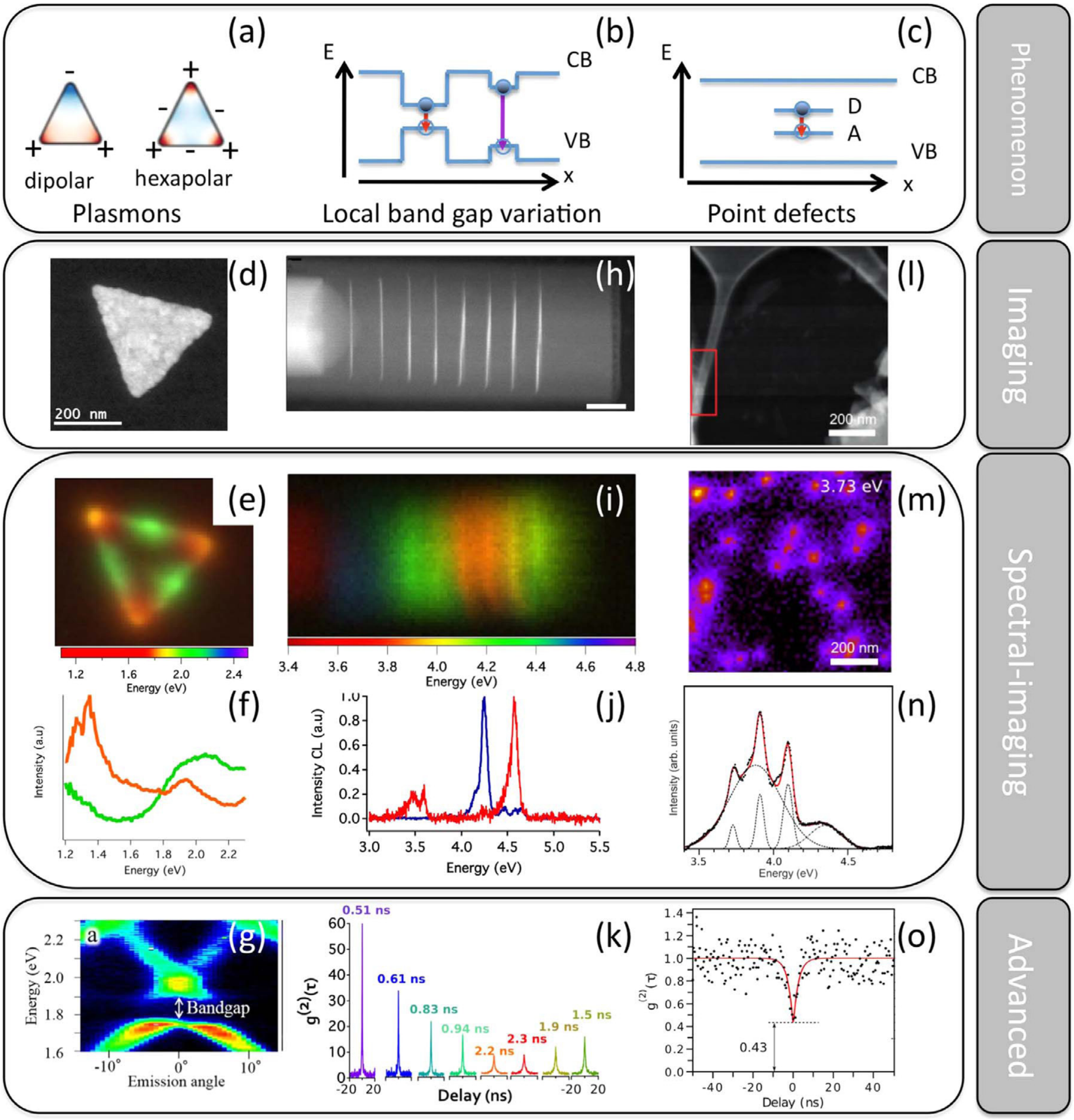

Fig. 1. Summary of the main physical properties that are efficiently investigated in STEM-CL (a–c), and how different information can be obtained by this technique (d–o), as described in detail in this review. (a). Plasmons emission arises from the deexcitation of plasmonic waves, which are essentially charge density waves. The figure shows the surface charge distribution for a triangular prism for one of the degenerate dipolar modes and for the hexapolar mode. After [3], reprinted with permission. (b). Local optical transition energy (optical band gap) variations in semiconductors. The optical property variations might arise from a local change in composition or stress, changing the "bulk" energy band gap, or from quantum confinement. In either case, electron-hole pairs will recombine where locally the energy (E) of the excited states (here schematised as the energy difference between the conduction band CB and the valence band VB) is the lowest (here along an arbitrary axis x). (c). Point defects and related atomic-like defects. Point defects or atom inclusions in a relatively high band gap material can behave as an idealised two levels system lying in the gap of the host material. (d). HAADF image of a 360 nm wide silver triangle. (e). CL polychromatic maps (see text) showing the spatio-spectral behaviour of plasmon modes; this can be directly correlated to the morphological information in (d). (f). Two typical spectra have been extracted at the tip (orange) and the side (green) of the prism. (e). (g). Angle-resolved CL spectroscopy of a plasmonic band gap material consisting in a series of silver pillars. The periodicity induces a band gap that is directly detected in STEM-CL. (h). HAADF image of a series of GaN quantum discs (QDisk) (bright contrast) embedded in a AlN (dark contrast) shell. (i). Related polychromatic map, showing individual QDisk colour variation. (j): Spectra extracted on two different QDisks. (k). Time correlation functions taken at the centre of each disc allowing to determine the QDisks lifetimes (indicated close to the corresponding peak). (l). HAADF of an h-BN flake. Because the flake is very thin, its HAADF contrast is essentially null, to be compared with the CL contrast in (m). (m). Monochromatic image filtered at the energy of an individual defect, the signature of which is shown in (n). (o). Time correlation function displaying a dip indicating single photon emission. (d-f) adapted from [4], (g) from [5], (h–k) from [6] and (l–o) from [7]. Reprinted with permission.

electron-hole recombination occur (in the case of near band edge, NBE) and larger ones to the occurrence of excitonic recombinations or shallow defect recombinations. There are two main reasons for band gap modulation at the nanometer scale. The first reason might be a change of the material composition or characteristics - for example, a desired or undesired change of the value of x in an $In_xGa_{1-x}N$ material, or a change of the stress states that modify the local energy gap. The second reason might be some quantum confinement, i. e. the fact that the electron and hole wavefunctions can be confined when a semiconductor material embedded in a higher energy gap semiconductor has at least one of its dimension smaller than a typical exciton Bohr radius, which varies from tens of nanometers to tens of ångströms. The two effects, of course, can compete to change the local emission wavelength. Such band gap monitoring and engineering is of the utmost interest in many fields:

Please cite this article as: M. Kociak, L.F. Zagonel, Cathodoluminescence in the scanning transmission electron microscope, Ultramicroscopy (2017), http://dx.doi.org/10.1016/j.ultramic.2017.03.014