Prospects and challenges of cathodoluminescence imaging in solid-state devices: A brief review

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Abstract-
The prospect of cathodoluminescence (CL) imaging is evident in its multi-versatile application. For almost three decades, the use of CL imaging in solid-state research has evolved into a reliable characterization tool. In this paper, a chronological review on the theoretical dynamics of CL on semiconductor and nanoscale materials was presented. It was concluded that the optimization of the CL imaging process depends on the microstructural abnormally of the sample.

Key words: cathodoluminescence, imaging, electron, microscopy, energy

1. Introduction
The veracity of the cathodoluminescence (CL) imaging applications in various fields of science and engineering is becoming amazing by the day. Recent CL modifications present its robust physics and application. In recent times, the CL operating device is modified or optimized by introducing other optical framework to boost its functionality. For example, the correlations of light microscopy with electron microscopy have been reported to give efficient results [1]. However because of the shortcoming of the work is the rapid optical signal degradation under electron beam irradiation [2].

The principle of cathodoluminescence entails the focusing of high-energy electrons to bombard an insulating or semiconducting material to emit or release a beam of light. The beam of light is a long-wavelength ultraviolet, visible and infrared radiation. The quality of the cathodoluminescence depends on many factors not limited to wavelength, electronic transitions, quantum confinement, electronic structure, chemical bonds, intrinsic carriers density, alloy concentrations, temperature, impurities, absorption coefficient, diffusion coefficient, defects, concentration of the optical center, internal growth of material, diffusion length and band gap energy of the material. The chosen material or specimen is as important as the cathodoluminescence process. For example, specimens that have transition rare earth metals are susceptible to electron beam excitation because of its 3d electron shells. In this case and many more, the physics of the cathodoluminescence have suffered several set-back because electrons in its excited state are generally unstable. The cathodoluminescence (CL) may also be excited by X-rays generated in the specimen – leading to an increase in the volume of the CL excitations. This is also a basic shortcoming of the CL as a scanning or imaging tool. However, scientists have made considerable efforts to overcome some of the challenges by incorporating devices (e.g. spectrometer, DigiScan hardware) to boost the functionality of cathodoluminescence. Thonke et al. [3] postulated that the achievable spatial resolution in CL is governed by three main factors: (i) the beam diameter, (ii) the volume, where the electron energy is deposited and (e,h) pairs are generated, and (iii) the diffusion length of minority carriers and excitons.

Engelsen et al. [4] described three advanced techniques for cathodoluminescence (CL) spectroscopy that were developed. The first was the comparison method where a conductive plate or thin layers of a conductive phosphor powder were used to determine the power density...
of the impinging electron beam. The second technique is the Cathodoluminescence in a scanning electron microscope (SEM) or the scanning transmission electron microscope (STEM). CL –SEM or CL-STEM have been proven to be an efficient tool for characterizing bulk, thin film and nano-structures. Both techniques are used to obtain spatial resolution (when electron beam is position at specific sites to obtain spot mode spectra) or spatially averaged spectra (when beam is positioned to scan images of samples). Hence the third technique in the cathodoluminescence analysis is the combination of microscopy and spectrometry in a transmission electron microscope (TEM). The comparative method was adjudged to have an elaborate CL-efficiency. Contrary to the view of Engelsen et al. [4], no CL-type can be adjudged the best in recent times. For example, Thonke et al. [3] clarified that the shortcoming of the CL-SEM are basically its field-emitter-type cathodes. However, in recent times the newest generation of field emitter type microscope provides high current (~ 100 nA) and excellent image quality. Hence, the validity on which CL-type is more efficient is becoming inconclusive due to technological advancements.

In this paper, the theoretical formulation of fundamental CL principle was explained. The concept was extensively discussed using the semiconductors. Lastly, the effect of the CL process on nanoscale materials was discussed.

2. Theories and dynamic principle of Cathodoluminescence imaging

Recall that the CL occurs when high-energy electrons bombard an insulating or semiconducting material to emit or release a beam of light. The luminescence from CL is different from photoluminescence. The later generate one electron hole pair from one incident photon while the former can generate a few thousand electron holes from a 20 keV electron. In this section, the semiconductor is used to express the theories of semiconductor.

The CL process begins by exciting an electron from the valence band into the conduction band (Figure 1a). This process sparks up the emission of secondary electrons (SE), back scattering of electrons (BSE), electron absorption (EA). The ionization energy required to create one electron hole pair was postulated by Klein [5] as:

\[ E_i = 2.8E_g + M \]  

where \( E_g \) is the bandgap, \( M \) is the material dependent factor (0 < \( M < 1 \)). Equation (2) shows that the ionization energy is independent of the electron beam. In reality, the electron-hole pair generated during CL is in thousands. Hence, the neutrality condition is assumed where the number of electron excited into the conduction band is equal to the hole left in the valence band. This process is theoretically represented [6] as

\[ \int_{\varepsilon_b}^{\varepsilon_c} g_n(\varepsilon)f_n(\varepsilon)d\varepsilon + \sum_{\Delta} \frac{1}{e^{\frac{-\varepsilon_d-\zeta}{k_B T}}+1} = \int_{\varepsilon_b}^{\varepsilon_c} g_p(\varepsilon')f_p(\varepsilon')d\varepsilon' + \sum_{\Delta} \frac{1}{e^{\frac{-\varepsilon_a+\zeta}{k_B T}}+1} \]  

where as \( f_n(\varepsilon) \) is the Fermi function of holes, \( f_p(\varepsilon) \) is the Fermi function of electrons, \( \varepsilon_D \) is the electron energy in the conduction band at the donor level, \( \varepsilon_D \) is the electron energy in the conduction band at the acceptor level, \( \zeta \) is the chemical potential, T is the temperature, \( k_B \) is the Boltzmann constant, \( g_n(\varepsilon) \) is the density of electron states, \( g_p(\varepsilon') \) is the density of hole states.
The practical significance of equation (3) is that at large electron-hole pair, there are possibilities of having different carrier diffusion due to the physics of many bodies. The excited states become energetically unstable and relax by dropping down from the conduction band to the valence band (Figure 1b). This process is known as recombination and it emits CL, X-ray and Auger electrons (AE).

Uno et al. (2012) gave chain of equation explaining an ir radiative recombination process for downward transition rate as:

\[ T_{k\rightarrow j} = T_0 \exp \left( \frac{-2R_k}{\alpha} \right) \]

\[ T_{k\rightarrow j} = T_{j\rightarrow k} \frac{d_{k-n_k(t)}}{d_{j-n_j(t)}} \exp \left( \frac{E_k-E_j}{kT} \right) \]  

(3)

where \( R_k \) is the hopping distance determined by energy below \( E_k \), \( V_o \) is the attempt-to–escape-frequency of the \( 10^{12} \text{s}^{-1} \), \( \alpha \) is the absorption coefficient of the material at the energy of the incoming photon, \( E_k \) and \( E_j \) are the energies of states \( k \) and \( j \) respectively.

The upward energy transition was also written as:

\[ T_{k\rightarrow j} = V_o \exp \left( \frac{-2R_k}{\alpha} \right) \frac{d_{j-n_j(t)}}{\sum \left[ d_{j-n_j(t)} \right]} \]

(4)

(5)
Here the concentration of charge carriers at time ‘t’ was given as ‘n’, the recombination rate would be of the order $\Gamma_r n^{-3/2}$. This means that the recombination rate can be written as the product of the density of filled electron state $n$ and the probability $n^2$. Equations 4 – 6 typify a scenario where the intensity of the CL is dependent on many factors as stated earlier in the introductory part. For example, the presence of impurity changes the downward and upward transition rates, hence there is a creation of an additional energy states in the energy gap that changes the wavelength and the intensity of the light. This process provides a avenue for CL imaging to be more efficient in studying spatial distribution of the impurity in materials. At this point, the energy gap is dependent on the temperature of the specimen or semiconductor.

3. **Cathodoluminescence imaging: The semiconductor perspective**

The specific objectives for fabricating semiconductors in the nineteen-sixty's was to determine materials of high efficiency for radiative recombination. CL was used to understand the nature of radiative recombination. The common CL technique then was the voltage regulation of the CL [7-8] which was between 5 and 50 kV. Gergely (1960) worked on the semiconductor from phosphors compounds. The diffusion length and recombination velocity of the phosphor compound were 0.05-0.15 micron and $5 \times 10^3 - 5 \times 10^4$ respectively. Wittry and Kyser [8] extended the research to n-type GaAs semiconductor. The diffusion length was found to be between 0.5 and 4 micron. Despite the promising result that was obtained, the appearance of various thresholds on the GaAs semiconductor was an indication of a deeper physics. Sooner, the concept of saturation characteristics of blue cathodoluminescence in ZnCu semiconductor emerged [9] but with little understanding on the effect of the saturation characteristics on the radiative recombination. The earliest theoretical investigation on the saturation characteristics of blue CL was carried-out by Muto [9] using the Maiman's three level model. It was discover the phenomenon is triggered by the impurity level in the semiconductor. The impurity level sometimes may appear as minority carrier depending on the objective of the researcher. For example Boulou and Bois [10] worked on the minority-carrier lifetime in semiconductors and postulated that the pulse duration influences the cathodoluminescence decay in GaP. Earlier in 1975, Marciniak and Wittry [11] had postulated that the cathodoluminescence properties of GaAs, GaP, and GaAs1–xPx alloys are dependent on temperature. Specifically, the researcher [11] emphasized that GaP had crossover composition of $\sim 0.5 \text{ mole\%}$ at 30 and 300 °K. Hence the observation on the GaP semiconductors suggest that there was the need to further observe samples microscopically.

Among the salient discoveries in 1975 was the emergence of the simplest low-dimensional semiconductor i.e. quantum well [12]. The main observation was that the bandgap of the quantum well (QW) material determines the effective bandgap of the QW. Hence, the difference between the bandgap of two materials may be arise from the nature of material, thickness, or width of the QW. However, as different QW material emerged, the main question became how to determine the quality of low-dimensional semiconductors. Secondly, the bandgap of small samples e.g. of 1 monolayer cannot be accessed. 1 monolayer (1ML) is the thinnest complete layer of the semiconductor. In 1987, there was a major breakthrough using the low-voltage range of CL imaging to unravel the properties of ML-flat areas larger than $\sim 0.5 \mu m$ can be accessed. For example, Petroff et al. [13] documented ML-flat island sizes of $\sim 1 \mu m$ for AlGaAs/GaAs system while Bimberg et al. [14] reported ML-flat island sizes of 6-8 $\mu m$. Gustafsson and Kapon [15] emphasized that under varying temperature and resulting features, it
is difficult to interpret the CL images because at certain temperature, the images show complimentary behaviour. Gustafsson and Samuelson [16] the point at which the CL images may be misinterpreted is where there is described the scenario. What is most important is that the 110 K images still show a variation in the density of smaller islands of 4 and 5 ML.

Kanaya & Okayama [17] mathematically described the range of the incident electrons on a specimen (crystal) as:

\[
R_o(\mu m) = \frac{0.0276A}{\rho^{0.889}E_o^{1.67}}
\]

where \( E_o \) (keV) is the incident beam energy, \( A \) (g/mol) is the atomic mass, \( \rho \) (g/cm\(^3\)) is the density and \( Z \) is the atomic number.

The scientific significance of equation (6) is the possibility of conducting depth profiling. This singular advantage makes CL a better characterization technique. Also, equation (6) can be used to interpret intrinsic and extrinsic CL results. For example, Akasaki et al. [18] discovery on the cathodoluminescence imaging of GaN:Mg sample show that the longer the beam in the scanning electron microscope, the brighter the blue luminescence appeared to be. In recent times, scientists have shown the different interpretations of the intrinsic and extrinsic CL on the GaN compound [19-20]. However, the emerging physics of the CL show the triviality of equation (1). For example, electron beam interaction effect and carrier diffusion on CL images are topical in CL application. Drouin [19] presented a study on the carrier diffusion lengths on self-assembled quantum dots (QDs) by low-voltage cathodoluminescence. The researcher was able to show effect of carrier diffusion on CL images of GaN materials. Hence, the dynamic physics of the CL imaging is very elaborate considering the present and future applications.

4. Cathodoluminescence analysis of nanoscale environment

The application of nano-technology is particularly interesting beginning from the semiconductor nanowires or nanocolumn [21-22].

Glen et al. [2] demonstrated cathodoluminescence of nanoparticles of semiconductors. Comparative analysis of secondary and cathodoluminescence images of LuAG:Ce clearly showed that some of the smallest nanoparticles in the material were not detectable in CL at practical integration times of ~ 90 µs / pixel. Figure 1 a-b further expantiate on the inadequacies of the CL imaging. The purple boxes show spaces where nanoparticles (NPs) cannot be located and the red boxes show regions where NPs can be located. One of the motivations of nanostructure, e.g. crystalline material is its tendency to significantly its efficiency to emit light [23]. This property of nanoscale environment is stem from the physics of its optical local density of states (LDOS) which is mathematically related by the Fermi Golden Rule (Grynberg et al. 2010). Advance in science, has shown the connection of the LDOS to the cathodoluminescence (CL) concept in the field of nanophotonics [24]. This discovery is currently used to study the optical properties of materials [25]. However, this technique is limited by the incoherent background (of transition radiation) that is induced simultaneously by the electron beam. This challenge led to the introduction of Hanbury-Brown-Twiss (HBT) intensity interferometer to the CL-STEM [26]. Moerland et al. (2016) coined the experimental set-up as Hanbury-Brown-Twiss (HBT) CL detection scheme. This technique has demonstrated huge successes in analyzing nano materials. For example, it was used to examine the photon anti-bunching in nanodiamond nitrogen vacancy centers [27]. However, its imperfection has led to the new concept of time-resolved cathodoluminescence microscopy that has also been limited by low effective current in the pulsed beam. Although experimentalists have shown that the introduction of beam-blanking can resolve the challenge [28], it is still unclear if CL can be
used to analyze nano-material that is below the diffraction limit or extremely low typical emitter lifetimes.

Figure 2: SEM image of (a) closely packed nanoclusters (b) reanalysed nanocluster

Thonke et al. [3] observed the nanoscale characterisation of semiconductors by cathodoluminescence to clarify radiative recombination processes in semiconductors with so-called direct or indirect bandgap.

4. Conclusion

The theoretical implication of CL modification to obtain quality imaging is a direct function of the sample and supportive framework. The microstructural abnormality in the sample is a direct function of the individual elements and elemental composition of the material. The CL performance on nanoscale material is quite unique judging from the current understanding of the predefined set-up. However, there are lots of optimization opportunities for the CL process to advance on characterizing complex samples like the cuprates superconductors.

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Reference

[1] Modla, S.&Czymmek, K. J. Correlative microscopy: A powerful tool for exploring neurological cells and tissues. Micron 42, 773–792 (2011).
[2] Glenn D. R., Zhang H., N. Kasthuri, R. Schalek, P. K. Lo, A. S. Trifonov, H. Park, J.W. Lichtman and R. L. Walsworth, Correlative light and electron microscopy using cathodoluminescence from nanoparticles with distinguishable colours, Scientific Reports 2: 865 (2012)
[3] Thonke K, Tischer I, Hocker M, Schirra M, Fujan K, Wiedenmann M, Schneider R, Frey M and Feneberg M. Nanoscale characterisation of semiconductors by cathodoluminescence, IOP Conf. Ser.: Mater. Sci. Eng. 55 012018 (2014)
[4] Engelsen Daniel, Fern George R., Harris Paul G., Ireland Terry G. and Silver Jack, New Developments in Cathodoluminescence Spectroscopy for the Study of Luminescent Materials, Materials, 10, 312 (2017)
[5] Klein C. A. Bandgap Dependence and Related Features of Radiation Ionization, J. Appi. Phys. 39 2029 (1968)
[6] Uno E. Uno, Moses E. Emetere, Isah K.U and Umaru Ahmadu, On the Effect Of Electron-Hole Recombination In Disordered GaAs-AA1-XAlAs Multi-quantum Well Structure. International Journal of Fundamental Physical Sciences, 2 (4), 52-57, (2012)

[7] Gryenberg G., A. Aspect, and C. Fabre, Introduction to Quantum Optics: From the Semi-classical Approach to Quantized Light (Cambridge University Press, 2010).

[8] Wittry David B., and Kyser David F., Measurement of Diffusion Lengths in Direct-Gap Semiconductors by Electron-Beam Excitation, Journal of Applied Physics 38, 375 (1967)

[9] Muto J., Kamiyama M., Namba S., Science paper ICPR, 62, pp 99. (1968)

[10] Boulou M. and D. Bois, Cathodoluminescence measurements of the minority-carrier lifetime in semiconductors, Journal of Applied Physics 48, 4713 (1977)

[11] Marciniak H. C. and D. B. Wittry, Cathodoluminescence of GaAs1−xPx alloys, Journal of Applied Physics 46, 4823 (1975)

[12] Dingle, R., Wiegmann W. and Henry C.H. Quantum States of Confined Carriers in very Thin AlxGa1-xAs-GaAs-AlxGa1-xAs Heterostructures. Physics Rev. Lett. 33, 827-830. (1974).

[13] Petroff PM, Cibert J, Gossard AC, Dolan GI, Tu CW Interface structure and optical properties of quantum wells and quantum boxes. J. Vac. Sci. Technol. B 5, 1204-1208 (1987).

[14] Bimberg D, Christen J, Fukunaga T, Nakashima H, Mars DE, Miller JN Cathodoluminescence atomic scale images of monolayer islands at GaAs/GaAlAs interfaces. J. Vac. Sci. Technol. B 5, 1191-1197 (1987).

[15] Gustafsson Samuelson L., Cathodo-luminescence imaging of quantum wells: The influence of exciton transfer of the apparent island size. Phys. Rev. B 50, 11827-11832 (1994).

[16] Gustafsson Anders and Eli Kapon, Cathodoluminescence in the scanning electron microscope: application to low-dimensional semiconductor structures. Scanning Microscopy 12, (2), 285-299 (1998)

[17] Kanaya K. & Okayama S. Secondary electron emission due to primary and backscattered electrons, J. Phys. D: Appl. Phys. 5 43-58 (1972)

[18] Drouin D., Characterization of semiconductor materials using low voltage Cathodoluminescence and Monte Carlo simulation, Proceedings of Microanalysis Society http://www.microbeamanalysis.org/ ISBN 978-0-7334-3069-5 (2011)

[19] Aramide, F. O., Ibitoye, S. A., Oladele, I. O., & Borode, J. O. (2009). Effects of Carburization Time and Temperature on the Mechanical Properties of Carburized Mild Steel, Using Activated Carbon as Carburizer. Materials Research, 12(4), 483–487. https://doi.org/10.1590/S1516-14392009000400018

[20] Boguslawski P., Briggs E. L., and Bernhole J., Phys. Rev. B 51, 17255 (1995).

[21] Plante M. C. and R. R. LaPierre, Growth mechanisms of GaAs nanowires by gas source molecular, J. Crys. Grow. 286, 394 (2006).

[22] C. Chen, M. C. Plante, C. Fradin, R. LaPierre, Layer-by-layer and step-flow growth mechanisms in GaAsP/GaP nanowire heterostructures, J. Mat. Res. 12, 11 (2006).

[23] Awopetu, O. O., & Ayodeji, S. P. (2008). Effect of Type of Workpiece Material on Chip Formation Process, 11(3), 181–186. E. Afoakwa, Cocoa Production and Processing Technology. 2014. Akasaki, T. Kozowa, K. Hiramatsu, N. Sawak, K. Ikeda and Y. Ishii, J. Lumin. 40-41, 121(1988).

[24] García de Abajo F. J., “Optical excitations in electron microscopy,” Rev. Mod. Phys. 82, 209–275 (2010).

[25] K. Takeuchi and N. Yamamoto, Visualization of surface plasmon polariton waves in two-
dimensional plasmonic crystal by cathodoluminescence, Opt. Express 19, 12365–12374 (2011).

[26] Meuret S., Tizei L.H.G, A. Losquin, R. Bourrellier, L.F. Zagonel, M. Tencé, A. Zobelli, O. Stéphan, M. Kociak, Advances in Scanning Transmission Electron Microscope Cathodoluminescence, Microsc. Microanal. 21 (3), 1687-1688 (2015).

[27] Tizei L. and M. Kociak, “Spatially resolved quantum nano-optics of single photons using an electron microscope,” Phys. Rev. Lett. 110, 153604 (2013).

[28] Moerland J. Robert, I. Gerward C. Weppelman, Mathijs W. H. Garming, Pieter Kruit, and Jacob P. Hoogenboom, Time-resolved cathodoluminescence microscopy with sub-nanosecond beam blanking for direct evaluation of the local density of states. Optics Express, 24 (21) 24760 (2016)