

An advanced cathodoluminescence facility in a high-resolution scanning electron microscope for nanostructure characterization

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We report a state-of-the-art cathodoluminescence (CL) facility attached to a high-resolution scanning electron microscope (HRSEM), installed recently at the Saha Institute of Nuclear Physics, Kolkata for the study of opto-electronic properties of nanostructured materials. In this note, we present the technical details of such a CL-SEM facility along with some experimental results. We also demonstrate that the high spatial resolution spectroscopy and imaging capability of a CL-SEM system can be utilized as an ideal tool for nanophotonic research.

Interaction of kiloelectronvolt (keV) electrons with matter can produce a variety of emitted signals such as secondary electrons (SE), backscattered electrons (BSE), X-rays and photons in ultraviolet (UV)-visible and infrared (IR) range. The last process, i.e. emission of light induced by a stream of electrons (historically called as ‘cathode ray’) is known as cathodoluminescence (CL)¹, defined analogously with other luminescence processes, such as photoluminescence (PL) (light emission induced by photons). The different signals arising due to the interaction of energetic e-beam delivered from a scanning electron microscope (SEM) with the specimen can be monitored using specific detectors. All conventional luminescence techniques operate by creating electron–hole pairs via some external excitation source (apart from electrons/photons as mentioned above, other excitation sources may be X-rays, γ -rays, ions or any other energetic charged particles), which subsequently recombine to produce a photon of characteristic energy (equal to the differences of the energy between the different excited states involved in a particular transition). For cathodoluminescence in scanning electron microscope (CL-SEM), high spatial resolution is a key feature when compared to other local probe luminescence techniques such as micro-photoluminescence (μ PL), scanning near-field optical microscopy (SNOM) and scanning tunnelling luminescence (STL).

Luminescence induced by electrons as excitation source (CL) has many advantages over luminescence based on photons as excitation source. As, for example, while one electron–hole pair is generated by every incident photon (in case of PL), a 100 eV electron generates more than

hundred electron–hole pairs (in the case of CL). As charged particles can be easily manipulated by applying suitable electromagnetic lens or lens assembly, one can have an extremely small probe of only few nanometres. That is, in a high-resolution scanning electron microscope (HRSEM), such an electron beam can be scanned and focused over a surface area ranging from few nanometres to a micrometre scale, thus yielding capability of providing information on high spatial resolution CL. Moreover, by varying the energy of the electron beam, one can probe different depths (nm to μ m) of a sample, giving depth-resolved luminescence information. So, site-specific spectroscopy and photon-mapping in addition to the routinely available morphological information from SE imaging make CL-SEM an excellent tool for studying optical properties of individual nanostructures or assembly of nanoparticles located either in dispersed condition on the top surface of a substrate or buried in the sub-surface.

Basic layout of the CL-SEM set up

The CL-SEM facility described here was designed at the Saha Institute of Nuclear Physics (SINP), Kolkata and was custom fabricated by Carl Zeiss, Germany and Gatan, UK, by integrating two main units, namely a field emission gun SEM (SUPRA 40, Zeiss) and an optical detection unit (MonoCL3, Gatan) consisting of a light-collecting paraboloidal mirror, optical monochromator followed by a photon detector and photon-counting electronics. The Gatan MonoCL3 is operated by a Gatan Digital MicrographTM software. After successful installation of the SEM, the CL system was attached to

it through one of the ports of the SEM chamber, custom fabricated for attachment of the optical monochromator and detectors assembly. It took a significant amount of time and effort in calibrating, standardizing and precisely tuning the system to detect luminescence even from specimens with low quantum efficiency such as silicon. Figures 1 and 2 show the schematic view and actual photograph of the installed CL-SEM set-up.

Technical details of the CL-SEM facility

Configuration of the SEM unit

The SEM from Carl Zeiss (Supra 40 series) consists of a high stability Schottky field emission (FE) electron gun system followed by an electron beam column with a single condenser, resulting in a cross free beam path to get good contrast/brightness even at low kilovolt (kV) operation. The microscope was equipped with eucentric goniometer stage motorized in five axes (x , y , z , tilt and rotation). The electron accelerating voltage can go from 0.1 to 30 kV, whereas beam current ranges from 0.1 to 40 nA. The chamber pressure was maintained below 1×10^{-5} mbar by a turbo pump backed by a rotary pump having oil trap and oil mist filter that guarantees contamination-free vacuum environment. The field emission gun was kept at UHV (pressure level 10^{-10} mbar) by an ion pump (nominal pumping speed for dry N_2 is 53 l/s). The SEM was equipped with high efficiency annular in-lens SE detector integrated within the column (in addition to a chamber SE detector) and backscattered detector (BSD) (retractable under vacuum). Using commercially purchased

TECHNICAL NOTE

carbon film containing gold particles (standard sample used for resolution test) resulted in a resolution of 1.0 nm at 20 kV and 2.1 nm at 1 kV electron beam of our installed FESEM.

Construction of the optical detection unit

Light collection mirror: Gatan MonoCL3 system uses a retractable, diamond-turned, paraboloidal mirror containing a 1 mm hole at the centre of the mirror. Actual photograph of the mirror is shown

in Figure 3. The mirror was inserted manually to a position directly beneath the pole piece of SEM so that the electron beam passes through the hole of the mirror. The passage of the electron beam through the central position of the hole was confirmed by observing the SE image of the hole.

Photon detection: Peltier-cooled high-sensitivity photomultiplier tube (HSPMT) sensitive in the optical range 160–930 nm was employed to collect photons. The wavelength range for maximum re-

sponse for these grating is 300–800 nm. Another high-sensitivity liquid nitrogen-cooled germanium detector operated at a constant bias of -250 V was also used. The germanium detector has its spectral response in the range 800–1800 nm with a nominal responsivity of 5×10^9 VW^{-1} . The collected light was guided through a hollow aluminum tube attached to the paraboloidal mirror to the detector or to the monochromator.

The monochromator: The Gatan MonoCL3 system contains a chamber-mounted Czerny–Turner optical monochromator of focal length 300 nm. From the schematic diagram (Figure 1), we can see two lenses, one before the entrance slit mirror and another after the exit slit mirror. They are made of Spectrosil B fused quartz, which has high transmission ($>85\%$) from 170 to 2200 nm wavelength. The focal length was matched to the light path. There are two slits, one entrance and the other exit, which can be increased or decreased depending upon the luminescence efficiency of the specimen under consideration. The 1 mm slit opening allows a band pass of 2.7 nm. An Oriel 1200 lines/mm diffraction grating blazed at 500 nm and another with 600 lines/mm blazed at 1200 nm are

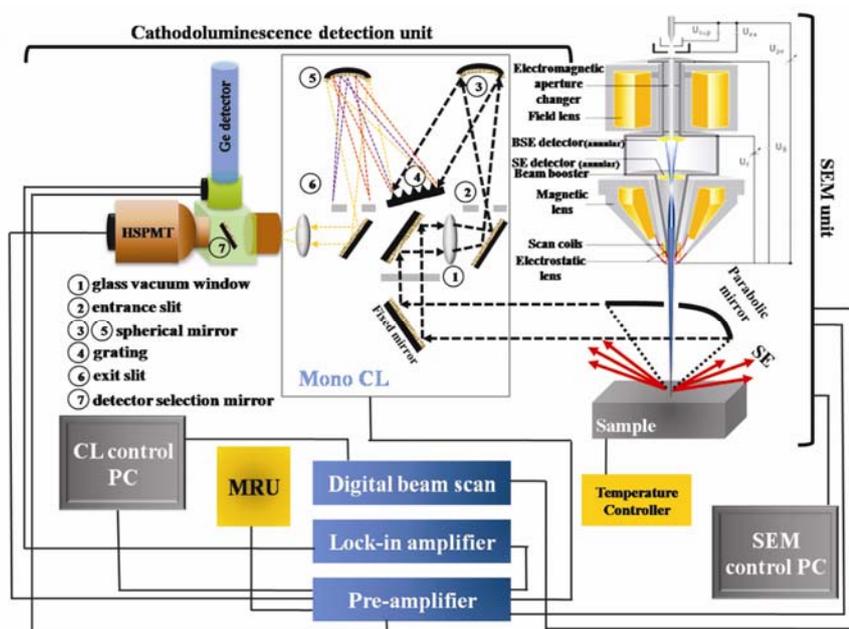


Figure 1. Schematic diagram of the cathodoluminescence in scanning electron microscope (CL-SEM) system.



Figure 2. Photograph of the CL-SEM system installed at the Saha Institute of Nuclear Physics, Kolkata.



Figure 3. CL parabolic mirror (views from top and bottom).

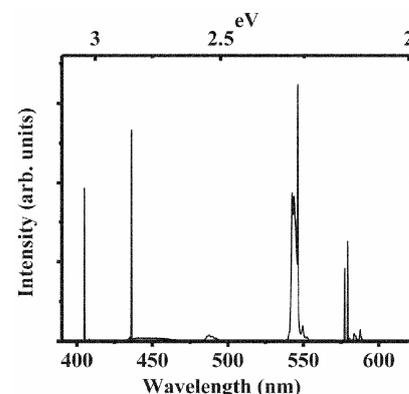


Figure 4. Calibration lamp spectra with entrance and exit slit width of $100 \mu\text{m}$.

used. The system was calibrated using 404.66 nm mercury spectral line of an inline discharge lamp. The very sharp line at 404.66 nm was fitted with a Gaussian and FWHM was calculated (spectra shown in Figure 4). In this way the instrumental resolution for a slit width of 100 μm (both entrance and exit) was found to be 0.2308 nm.

The width of the monochromator slits plays an important role in determining the maximum spectral resolution: the smaller the slit width, the greater the system resolution. However, reducing the monochromator slit width reduces the total light throughput of the system and, thus, the monochromator slit widths was selected to achieve the spectral resolution required while maintaining optimum throughput. The effect of increasing the slit width is dependent on the source image in the slit plane and the source spectrum.

Signal processing software

The Gatan MonoCL3 system was controlled by using the Digital Micrograph™ software. When a HSPMT is used, the software reads the output of HSPMT and in case of Ge detector it reads the output of the lock-in amplifier. All the spectra presented here were taken in the serial mode, i.e. the grating was positioned for a particular wavelength and the reading taken for a length of time which is known as dwell time, before the grating was moved to the next wavelength by a stepper motor. The starting wavelength, range of wavelengths sampled, number of steps and dwell time all are user defined within the software environment. The photon counting may be done in two ways: either in the total photon count mode or in counts per second (cps) mode.

Cryogenic stage arrangement

The Gatan-made (model: CF302M) continuous flow cooling stage as shown in Figure 5 consists of a side arm attachment (CF302DF) and a remote nitrogen Dewar for doing CL measurements at liquid N_2 (LN_2) temperature (78–300 K). The CF302M cold module stage inside the SEM analysis chamber was connected to the LN_2 Dewar outside the chamber through capillary tubes as inlet and outlet paths of the LN_2 flow by making feed

through seals on one of the ports of the SEM. Seals made of thin Indium foil were used for this purpose. With the CF302DF side arm attachment, nitrogen gas from the Dewar source was forced through the heat exchanger coil in the LN_2 Dewar, and flowed to the stage before being vented to the outside at the gas exhaust. The nitrogen gas from the Dewar was regulated between 0 and 20 psi and connected to the gas nozzle on the Dewar top. The temperature was monitored using a temperature controller (SmartSet Model: 900). This allows a temperature sensor to be read and temperature to be controlled by applying electrical power to a heater. Thus the sample can be held at any temperature between ambient and base temperature with minimum instability.

Setting the specimen at the focal point of the mirror

In order to allow the scattered light originating from the CL process to be

collimated through the hollow aluminum tube, the region of interest on the surface of a sample under study should ideally be located at the focal point of the mirror. So, to acquire a meaningful CL spectroscopy and or imaging data, the important first step is to set this focal point by maximizing the collected signal (as recorded directly from the CL detector output) according to the following procedure: the mirror focal point was kept generally approximately 1 mm below the bottom of the mirror to ensure its collection efficiency to be the largest as a first step of coarse adjustment. Then for fine adjustment, the height of the sample was varied several times with digitally controlled small step sizes so long as a brightest spot of the shape shown in Figure 6b was detected on the CL-controlled computer monitor from the luminescent portion corresponding to the SE image (Figure 6a) of the area of the sample set at low magnification. If needed, a small adjustment can also be made simultaneously by the small translation of the sample in the x - y plane.

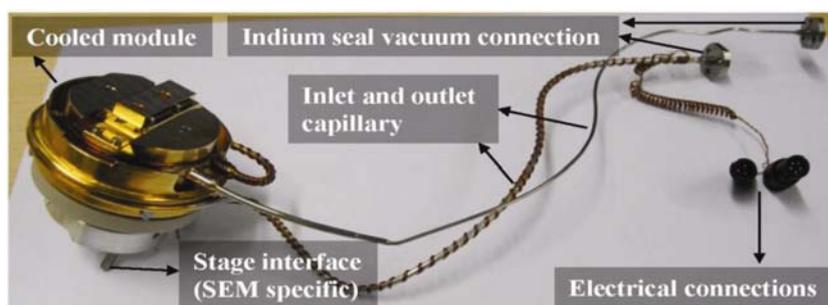


Figure 5. Cryogenic stage module along with its different components.

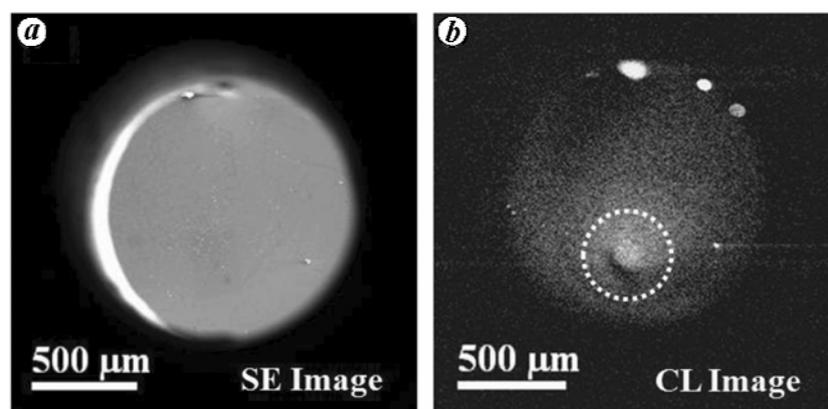


Figure 6. **a**, SE image at the lowest possible magnification of the SEM. The circular hole is the aperture of the mirror (1 mm diameter). Beneath this is the specimen under consideration. **b**, Panchromatic CL image after height adjustment between the mirror and sample surface. The brightest zone encircled by white dots is the focal position of the specimen commonly called as hotspot.

This procedure was followed at the beginning of each session to align the system for optimum signal detection which ensures that the scattered light from the region of interest after reflecting from the mirror is correctly collimated.

Operational modes of a CL system

The CL equipment can be operated in three main modes. The first is the panchromatic imaging mode. In this mode the electron beam is scanned to form an image from the output signals contributed by all the emitted wavelengths of CL from a sample. So in the CL image the contrast is caused by the variation of the photon counts or light intensity between any two points. The second mode is the monochromatic CL imaging mode, where the CL image consists of photons with particular frequency or light of particular wavelength. In this case the beam is scanned and a pixel-by-pixel image is formed, but a dispersive element is included between the CL collector and the detector. As a dispersive element a diffraction grating monochromator has been used (in our case either 1200 lines/mm or 600 lines/mm), since this enables a desired spectral wavelength to be selected with ease. The third mode is the CL spectrum mode. In this case no image is formed, the electron beam is scanned over the area of interest on the specimen or is kept at a fixed point (spot mode) and the emitted luminescence spectrally analysed. Instead of being set to a fixed wavelength, the monochromator runs serially through a range of wavelengths and the CL intensity is measured as a function of wavelength.

Application of CL

Band structure information

CL of bulk InP: We used a piece of commercially available single crystalline InP(100) wafer doped with Zn with a dopant concentration of $\sim 10^{18} \text{ cm}^{-3}$. As reported in the literature², low temperature CL spectra of InP exhibited two closely spaced bands at 1.41 and 1.38 eV. These peaks are attributed to band-to-band and band acceptor transition respectively. We found only one peak at 1.42 eV at room temperature (Figure 7b), which is consistent with the results reported earlier.

With this measurement we also verified the response of our HSPMT in the high-wavelength range.

Luminescence from low-dimensional semiconducting structures

CL from single quantum well GaN on Sapphire: We also checked the performance of our system with a well-known highly luminescent sample, like a single quantum well GaN grown on sapphire substrate. We observed two major CL peaks at wavelengths of 360 and 530 nm respectively. The 360 nm peak coincides with the band gap of GaN, which indicates that our system has been calibrated properly. The 530 nm peak is related to the defects present in the sample during growing. The spectra shown here (Figure 7a) were acquired with electron beam energy of 5 keV and 2 mm slit width (band pass of 5.4 nm).

Ultraviolet-visible CL from Ar⁺ beam-induced nanopatterned porous silicon

Figure 8a shows the micro structural details of self-organized ripple pattern formed after 60 keV Ar⁺ sputtering in crystalline Si (c-Si) at 60° angle of ion incidence. On the other hand, for normal angle of incidence no periodic morphology was found³. In such samples with self-organized periodic morphology, site-specific CL spectroscopy and imaging can yield a wealth of information concerning the influence of the variation of

microstructure on CL, the details of which can be found elsewhere⁴. The first spectrum (Figure 8b) shows strong room temperature luminescence bands in ripple patterned Si compared to a non-patterned amorphous Si (a-Si). Site-specific CL spectroscopy and imaging data indicate that while the top and front surfaces of the ripples (see schematic of Figure 8a) contribute predominantly to the red and near IR emission at 650 and 750 nm respectively, the back surface contributes mostly UV emission at 365 nm. We have demonstrated that the CL technique is sensitive to the presence of defects, dislocations and native oxides. Even the presence of a small amount of impurity or slight defect is reflected in the observed CL spectrum. After annealing at UHV we have found some ultra small Si ring-like structure as seen in the XTEM image⁴. This causes a blue shift of the CL peak from 650 to 575 nm.

We further analysed the CL map corresponding to the 365 nm emission peak from a larger area comprised of a sufficient number of ripples, as shown in Figure 9. Comparing the 365 nm CL line profile with the SE image profile as shown in Figure 9 (inset), we notice that maxima and minima of 365 nm emission occurs more or less in the back and top surfaces of the ripples, which is consistent with the higher intensity 365 nm emission from the spot spectra obtained from the back surface of the ripples. To the best of our knowledge such an efficient mapping of the spatial distribution of microstructures is only possible through CL measurements.

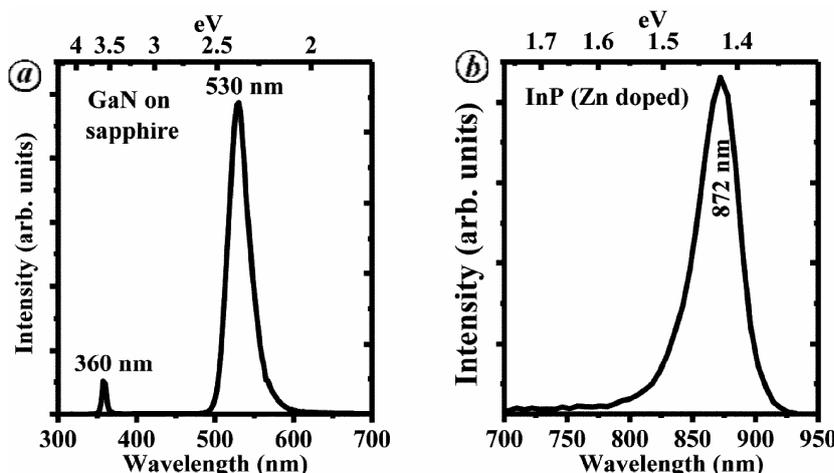


Figure 7. CL spectra of (a) single quantum well GaN on sapphire and (b) Zn doped InP. Both the spectra were taken at an electron beam voltage of 10 kV.

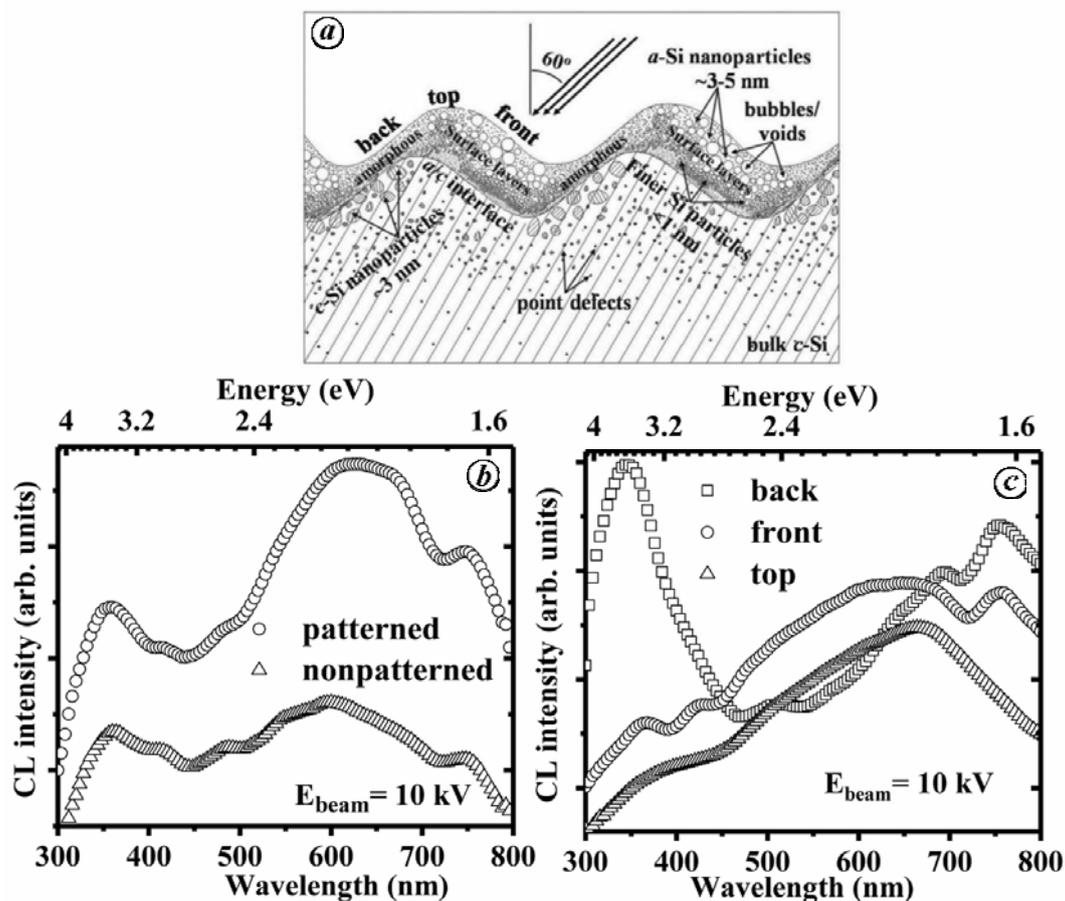


Figure 8. *a*, Cross-sectional view of microstructures of a 60 keV Ar⁺ bombarded Si ripples shown schematically. *b*, Room temperature CL spectra from patterned and non-patterned Si samples using electron excitation energy of 10 keV. *c*, CL spectra in spot mode taken from the back, front and top surface of the ripples.

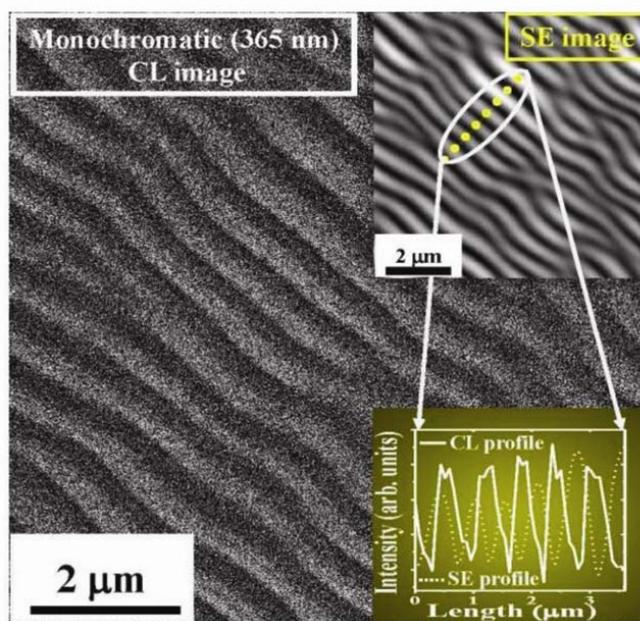


Figure 9. Monochromatic CL image using the 365 nm peak. (Inset, upper right corner) SE image from where CL map is acquired. (Inset, lower right corner) Comparison of the intensity profile of the 365 nm CL peak and the SE image grey level variation along the dotted line drawn on the SE image.

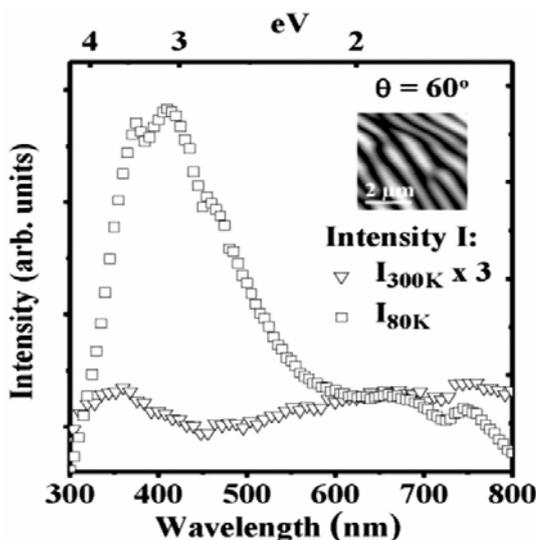


Figure 10. Enhancement of CL intensity with samples kept at LN₂ temperature. (Inset: Morphology of the sample from which spectra were taken.)

It is interesting to note that such an enhancement of CL intensity of porous silicon can be achieved when the CL is performed with the samples kept at LN₂ temperature, as shown in Figure 10.

Signature of surface plasmons in CL

When an electron is incident from vacuum onto the boundary of a material, it perturbs the electrons in the uppermost layers due to its external field and creates a polarization charge. This charge together with the incoming electron can be considered as an effective dipole. In case of a metal substrate the dipole can decay into two channels: direct emission into the far field (transition radiation) and generation of surface plasmons (SPs). CL is a promising technique for the spectroscopic study of localized SPs⁵. In CL, photon emission of the metal nanostruc-

ture under study is induced via high-energy electron beams, and collected using a suitable detection system, as described previously in our set-up. A unique feature of this is that by scanning the electron beam over the particle surface, the spatial profile of the modes can be mapped by collecting the light at the respective peak wavelength⁶. The same CL technique can also be employed for the excitation and study of propagating surface plasmon polaritons.

Conclusion

We have described the design, installation and performance of an advanced CL facility in a FESEM for characterization of nanostructure, that has been installed at SINP recently. Details of various components of the system have been discussed and we have demonstrated the

performance of the instrument using GaN on sapphire, Zn-doped InP and ion-implanted nano-patterned and non-patterned porous silicon. Apart from other promising luminescent materials, this facility is currently being used to study the spatial profile of SP modes from different low-dimensional metal nanostructures.

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