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Cathodoluminescence spectroscopy on lamellar metal and semiconductor gratings for nano-photonic devices

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ABSTRACT

Cathodoluminescence spectra of lamellar gratings have Gaussian profiles centered at ~600 nm independent of grating amplitude (0.1 to 4.6 microns), grating period (0.1 to 20 microns), material (metal, semimetal, or semiconductor), or e-beam energy, but the band blue-shifts somewhat with increasing e-beam current. A periodic modulation with wavelength appears for the higher grating amplitudes due to interference from simultaneously-emitting grating bars and grooves separated by 10s of microns, even though the excitation spot size is only ~10 nm. Unstructured surfaces have weak, flat, and featureless spectra, emphasizing the role of the grating in the emission process. Transition radiation and out-coupling of surface plasmons are eliminated on physical grounds as the source of the emission. We favor an e-beam-induced hot-electron current that excites electron hole-pairs over broad areas within the metal film as the most likely mechanism. This work relates to the selection of materials for nano-photonic devices.

Key words: Plasmonic electronic materials, Cathodoluminescence, Surface plasmon polaritons, nano-photonics.

INTRODUCTION

Nano-photonics refers to proposed devices in which generation, propagation, and manipulation of electromagnetic waves occurs within volumes small compared with corresponding free-space wavelengths. Surface plasmons, the electro-magnetic waves that propagate along the conductor/dielectric interfaces and that were originally studied via electron energy loss spectroscopy [1], are widely investigated [2][3] for potential use in sub wavelength optics, data storage, light generation, solar cells, microscopy, and bio-photonics. Though most nano-photonic research and development today uses optical methods, electron beam excitation of optical phenomena on nano-structured surfaces in principle allows superior spatial resolution comparable to focused e-beam spot sizes, i.e. ~10 nm. Surface structures themselves facilitate the out-coupling of light, which may be analyzed by cathodoluminescence (CL) spectroscopy[4][5][6][7].

Noble metals have been the mainstay of nano-photonic device research at visible and near IR wavelengths, but other materials with lower plasma frequencies offer

opportunities deeper in the IR. In this paper, we use CL spectroscopy to investigate simply structured surfaces formed of metals, semi-metals, and semiconductors.

Previous CL studies emphasized excitation and propagation of surface plasmon polaritons (SPP)[6]. It has been supposed that SPPs are excited locally, within the ~10 nm spot of the electron beam, whence they propagate to out-coupling structures such as gratings, to be converted to light collected by the CL system. The possibility that CL might be excited directly within the surface structures themselves, tens of microns away from the electron-beam spot as a result of electron-beam induced currents has not been suggested. We present evidence that such occurs, by demonstrating strong interference effects for CL originating from gratings that have periods large compared to SPP propagation lengths.

A characteristic of all previous CL studies of SPPs is that the signal attributed to surface plasmons sits on top of a strong and structured background spectrum. Suggested explanations have included surface contamination[4], electronic transitions within the metals band structure[4], collision of the impinging electrons with their image charges[4][2], transition radiation[2], and inverse photo-electron effect[8]. We find that none of these adequately explain our CL observations.

MATERIALS AND EXPERIMENTAL DETAILS

Lamellar gratings (period a = 7.5 or 20 micron, amplitude h = 0.1 to 4.6 micron) were photolithographically fabricated on silicon followed by optically thick metal depositions. Noble metals Au, Ag, semi-metals Sb and Bi, and bare silicon gratings (resistivities 8×10^{-5} and 1×10^{-6} Ω-m). Grating profiles were measured using a step profilometer. Two main grating configurations were investigated: gratings that completely covered quartered sections of 2 inch wafers and ones confined to 0.5 cm × 0.5 cm areas surrounded by smooth metal film. Additionally, small gratings were fabricated by focused ion beam (FIB) milling in optically thick gold films (a = 0.5 and 1 micron, h = 100 nm amplitude, 20 and 10 periods respectively).

CL was collected using a Gatan MonoCL3. The electron beam energy was typically set to 20 keV, but it could be varied. The results were independent of the area over which the beam was rastered, the emission being essentially instantaneous in comparison to the e-beam residence time within any particular surface feature. Grating orientations where chosen were either parallel or perpendicular to the axis of the parabolic light collector. Where possible, CL spectra were also collected with the electron beam outside the grating area, on surfaces of smooth unstructured metal, at various distances from the grating.

Fig. 1 presents a schematic of the CL excitation and collection geometry. The parabolic mirror collects the CL and sends it to the spectrometer through a light-guide. There is asymmetry in the set of the collection angles of the mirror about the electron beam hitting normally on the sample. The closest distance between the mirror and the sample is limited to 1 millimeter, which is the nominal position focal point of the parabaloid.

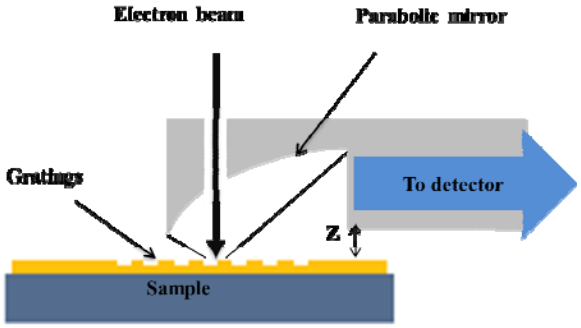

Figure 1: Schematic of SEM with CL collection parabaloid.

RESULTS AND DISCUSSION

Fig. 2 (left) presents normalized CL spectra for a = 20-micron Ag gratings of different h and perpendicular orientation. For small h, the CL spectrum is smooth and featureless. For higher h, a periodic modulation appears, whose period depends on grating amplitude and wavelength. The peak positions correspond to integral numbers of half wavelengths fitting into the depth of the grating grooves, i.e. $\lambda = 2h/m$, m integer. The triangle symbols indicate these positions, which are in good agreement with the spectral peaks though with variations in phase [7].

Fig. 2 (right) presents CL spectra for gratings made of other materials. The pattern of oscillations, as well as the overall envelop of the emission depends little on the material, nor do they depend on grating period. The main parameter affecting the period of the oscillations is the grating amplitude.

Fig. 3 (left) presents the interference peak position vs. wavelength for these gratings. The modulation period increases with increasing wavelength and with decreasing grating amplitude. The data fit well to the curves $\lambda = 2h/m$, m = integer which confirms that the modulation is the effect of interference from emissions emanating simultaneously from gratings bars and grooves. Since the period of the gratings is three orders larger than the e-beam spot size, the excitation volume for CL cannot be confined to the focused electron spot on the surface. Rather the excitation must be due to some far-propagating disturbance such as an electron beam induced current of hot electrons.

Fig. 3 (right) presents CL spectra for different electron beam energies for silver gratings with a = 20 μm and h = 4.6 μm. The spectral envelop, intensity, and modulation features are all essentially independent of e-beam energy. This observation argues against any CL mechanism that depends on the electron velocity, such as transition radiation. Equation (1) gives the transition radiation energy per unit solid angle, where n is the complex refractive index of the material, and ϕ is the emission angle relative to the surface normal [9].

$$\frac{dW_\omega}{d\Omega} = \frac{e^2 v^2}{\pi^2 c^3} \sin^2\phi \left| \frac{(n^2-1)\cos\phi}{n^2\cos\phi + \sqrt{n^2 - \sin^2\phi}} \right|^2 \qquad (1)$$

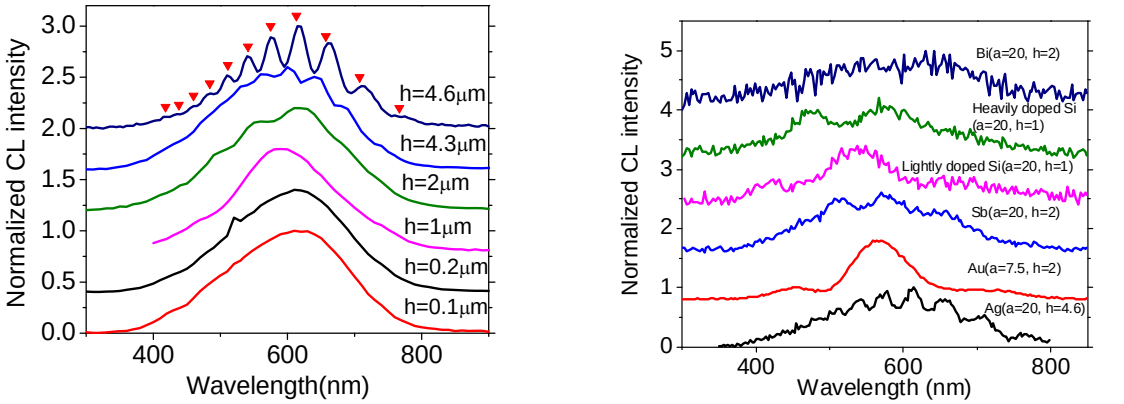

Figure 2: (**left**) CL spectra for 20-micron-period Ag gratings of different amplitudes, with grating bars perpendicular to the optical collection axis, and (**right**) CL for different other materials including Au, Sb, Bi, and doped Si. The flat featureless baseline amounting to about 10% of the signal has been subtracted and the resulting spectra normalized.

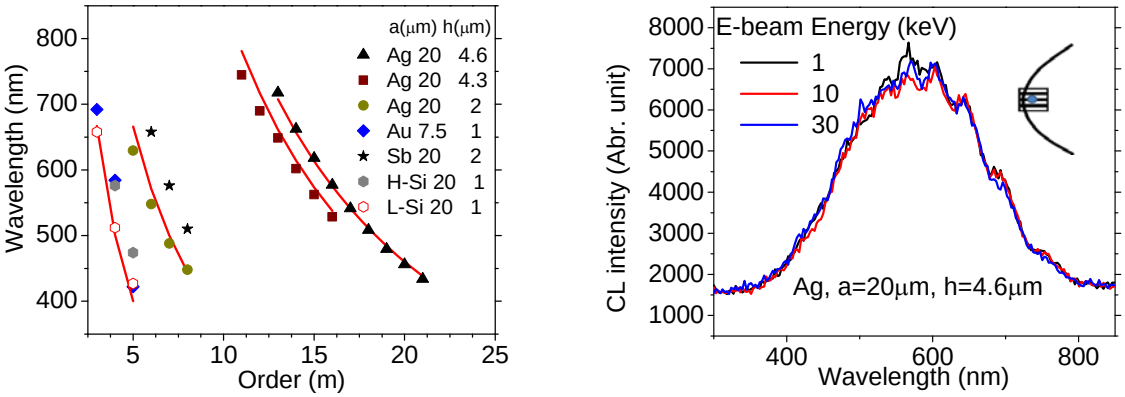

Figure 3 (**left**). Modulation peak wavelength vs resonance order, symbols are data and curves are calculated according to $\lambda = 2h/m$. (**right**). Raw CL spectra for silver gratings with different e-beam energy. The inset shows the grating-orientation and a schematic outline of the parabolic collection mirror, while the blue dot represents the e-beam spot.

Fig. 4 (left) presents calculated transition radiation integrated from -10 to 70 degrees collection angle for e-beam energies of 20 and 30 keV, which illustrates how the intensity of transition radiation depends strongly on electron velocity, in contrast to the experimental observations in Fig. 3 (right). Moreover, the peak of transition radiation for silver is at 350 nm, in contrast to our observed band centered at 600 nm wavelength.

Fig. 4 (right) presents CL spectra when the excitation spot is away from the FIB gold grating (a = 1 μm, h = 100 nm) in parallel orientation. There is little dependency in spectral intensity or shape on e-beam distance from the grating up to distances of 1 mm. Since SPP propagation lengths on gold at visible frequencies are on the order of 10 microns, there appears to be no contribution from SPPs, in contrast to prior studies [4][5][7].

Fig. 5 presents spectra from smooth Ag, Au, and bare Si surfaces. The emission band always observed near 600 nm when the e-beam excites on or near our grating samples is conspicuously absent when there is no grating. This indicates a strong role of the grating at least in outcoupling the CL signal, if not directly in its physical generation mechanism.

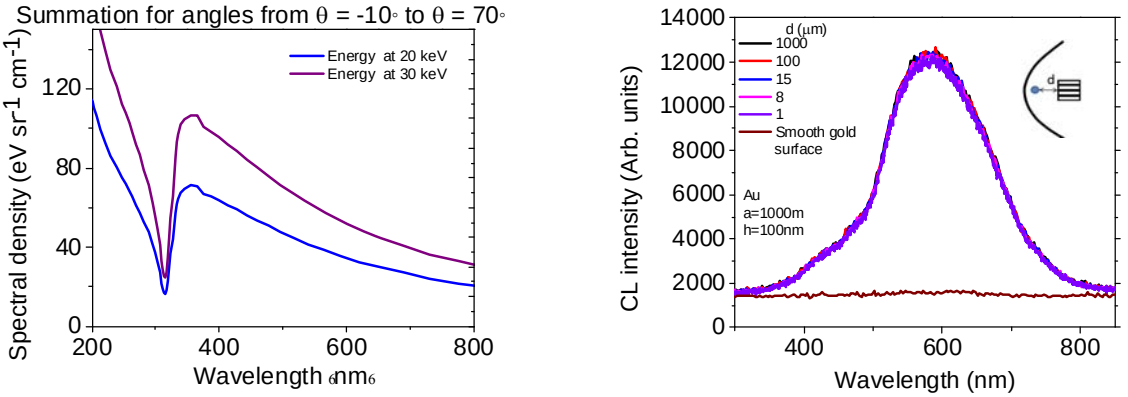

Figure 4: (**left**) Calculated spectrum of transition radiation integrated over collection angles -10 to 70 degrees for e-beam energy 20 and 30 keV, (**right**) CL spectra for electron beam excitation spot away from the FIB gratings (a = 1 micron, h = 100 nm). The spectrum for the smooth gold surface was taken on a portion of the same wafer that was broken off from the part that contains the FIB grating.

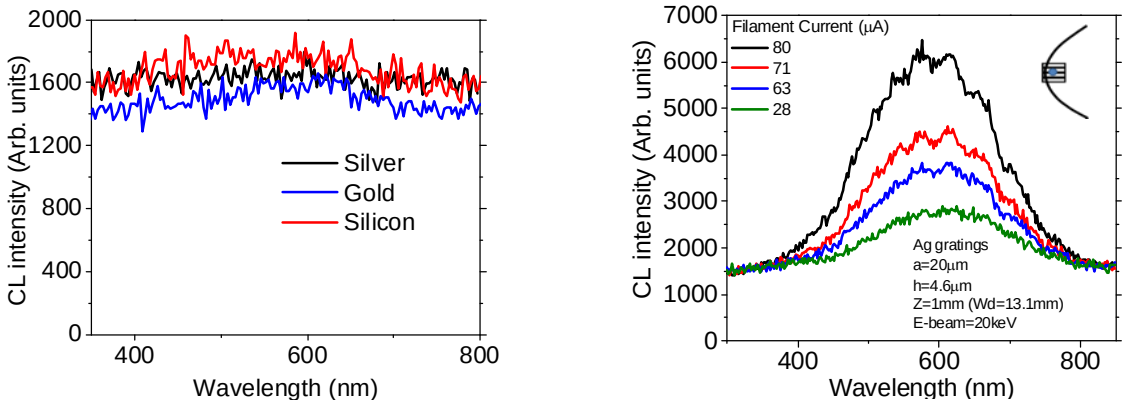

Figure 5: (**left**) CL spectra from smooth unstructured Ag, Au and Si surfaces. The spectrum is weak and nearly flat. (**right**) CL spectra for varying filament current on an Ag grating.

Fig. 5 (right) presents CL spectra for a 20-micron-period Ag grating with 4.6 micron amplitude as a function of filament current. The band blue shifts slightly and its intensity increases with current. Fig. 6 (left) shows that the intensity increase (baseline subtracted) depends non-linearly on current. Fig. 6 (right) presents the center wavelength and band width, calculated by the method of moments as a function of filament current for the Fig. 5 (right) data. Besides the blue shift with increasing current, there is also band narrowing.

CONCLUSIONS

An electron beam induced current of hot electrons can explain the simultaneous emission from a number of grating periods that are 10s of microns away from the excitation spot, which seems necessary to explain the observation of interference fringes. Absence of dependence on e-beam energy rules out any significant contribution from transition radiation, which would anyway peak at shorter wavelength. The CL spectra are remarkably independent of material (metal, semimetal, or semiconductor), which suggests no roll of band structure in the emission process. The only grating parameter

that the CL depends on is the grating amplitude, and then only in regard to the interference fringes that modulate the overall emission band. Yet the signal seems to depend on there being a grating, whose role may be merely one of out-coupling. Inverse photoelectric effect is expected to produce a band centered near 300 nm [8]. Surface contamination seems to have no roll since the CL shows little variation from sample to sample. A role for SPPs seems unlikely, since the distance from excitation spot to out-coupler (grating) can exceed by more than one order the characteristic propagation lengths of SPPs [4][5][7]. Intensity, band center, and band width do depend e-beam current, though these effects are unexplained so far.

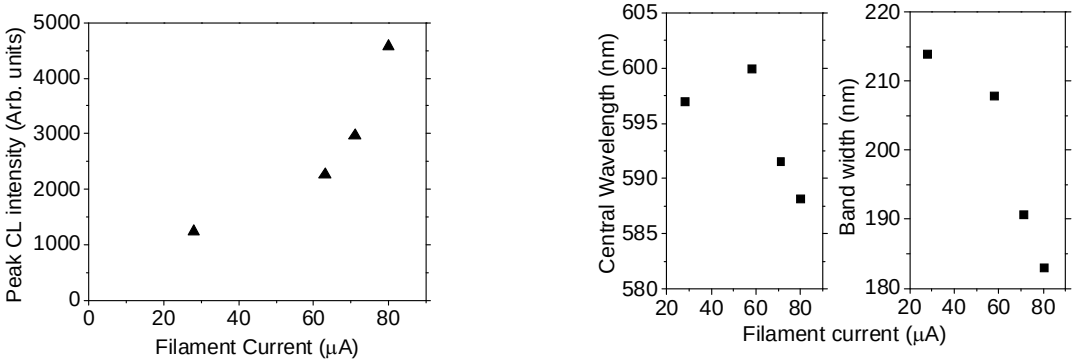

Figure 6: (**left**) Dependence of integrated CL intensity (background subtracted) on e-beam current. (**right**) Central wavelength and band width versus filament current.

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