# Cathodoluminescence study of silver and gold lamellar gratings

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## ABSTRACT

Cathodo-luminescence spectroscopy is performed on silver and gold lamellar gratings of period 7.5 or 20 microns for a range of grating amplitudes from 0.1 to 4.6 microns. The overall emission spectrum consists of a 400 nm wide band centered at ~600 nm which depends little on the grating amplitude, metal, or e-beam energy. For the larger grating amplitudes the emission spectrum is periodically modulated as a function of wavelength. Both the strength of the emission envelop and the depth and phase of the modulation depend on grating orientation with respect to the light collection axis, the distance of the excitation spot from the grating, and the distance between the grating and the collection optics. The modulation can be explained as interference of surface emission from grating bars and grooves. The origin of the emission remains unclear, as mechanisms of electron collision with image charge, transition radiation, surface contamination, and inverse photo-electron effect all fail to explain the observed spectrum. This work is relevant to the interpretation of cathodoluminescence studies of surface plasmons on structured metals for nano-photonic applications.

**Keywords:** Cathodo-luminescence, nano-photonics, Surface Plasmon Polaritons.

## 1. INTRODUCTION

Cathodoluminescence (CL) spectroscopy has been exploited to study excitation and propagation of surface plasmon polaritons (SPP) on structured metal films[1, 2, 3, 4] for nano-photonics applications. It has been supposed that SPPs are excited locally, within the ~10 nm spot of the electron beam, whence they may propagate to an out-coupling structure such a grating, to be converted to light that is collected by the CL optics. It has not been considered that CL might be excited directly within the out-coupling structures, 10s of microns away from the electron-beam spot, by electron-beam induced currents. We present evidence that such occurs, buy demonstrating strong interference effects for CL originating from gratings that have periods large compared to SPP propagation lengths.

A characteristic of all previous studies is that the signal attributed to surface plasmons sits on top of a strong and structured background spectrum. We assert that to properly interpret CL spectra in terms of surface plasmons, it is necessary to thoroughly understand the origin and characteristics of all background effects, since these tend to be the bulk of the signal. A variety of explanations have been suggested for the background including surface contamination[1], electronic transitions within the metal[5], collision of the impinging electrons with their image charges[1,2], transition radiation[6], and inverse photo-electron effect[7,8]. None of these effects adequately explain the CL spectrum we observe, whose intensity strongly depends on the presence of the grating.

## 2. EXPERIMENT AND RESULTS

Lamellar gratings were fabricated in silicon substrates by conventional photolithography. Grating periods of 7.5 and 20 microns were chosen with grating amplitudes that ranged from 0.1 to 4.6 microns. The silicon gratings were then given an optically thick coating of gold or silver using an electron-beam evaporator. Grating profiles were measured using a standard step profilometer.

CL was collected using a Gatan MonoCL3 in the wavelength range 200 to 1200 nm. The electron beam energy was typically set to 20 keV. The beam was rastered over areas of different dimensions, from single grating bars or valleys to areas that included multiple grating periods, by adjusting the magnification. We note that regardless of the area rastered over, the electron beam intersects the surface only on a ~10 nm spot at any instant. Nevertheless, we argue from our results that, due to electron beam induced current, excitation of luminescence may extend over tens of microns, with emission emanating from broad areas simultaneously. The CL is collected for different grating orientations with respect to the optical collection axis, and for different vertical separations between collection paraboloid and grating surfaces. The grating orientations 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 unstructured metal, at various distances from the grating.

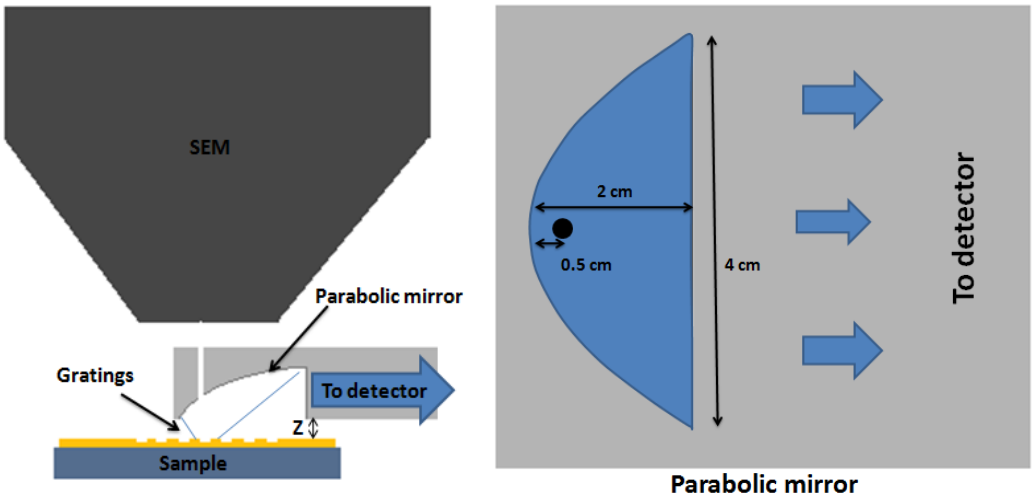


Fig 1: CL set up. (left) Side view schematic of SEM with CL collection parabaloid. (right) Top view of collection parabaloid with approximate dimensions.

Fig. 2 presents CL spectra for gratings of different amplitude $h$ for silver (20 micron period) and gold (7.5 micron period). Both materials show essentially the same spectral envelop extending from 400 to 800 nm, which argues against any emission mechanism involving electronic structure of the metal. Normalization has removed the dependence of the total CL intensity on grating amplitude, which was neither strong nor monotonic. For low amplitude gratings, the CL spectrum is smooth and featureless. For high amplitudes, a periodic modulation appears. The period of the modulation depends both 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 for the 20 micron period Ag grating. For the 7.5 micron Au grating, there is a phase shift between calculated and measured peak positions. The modulation peak positions are uncorrelated with the grating period.

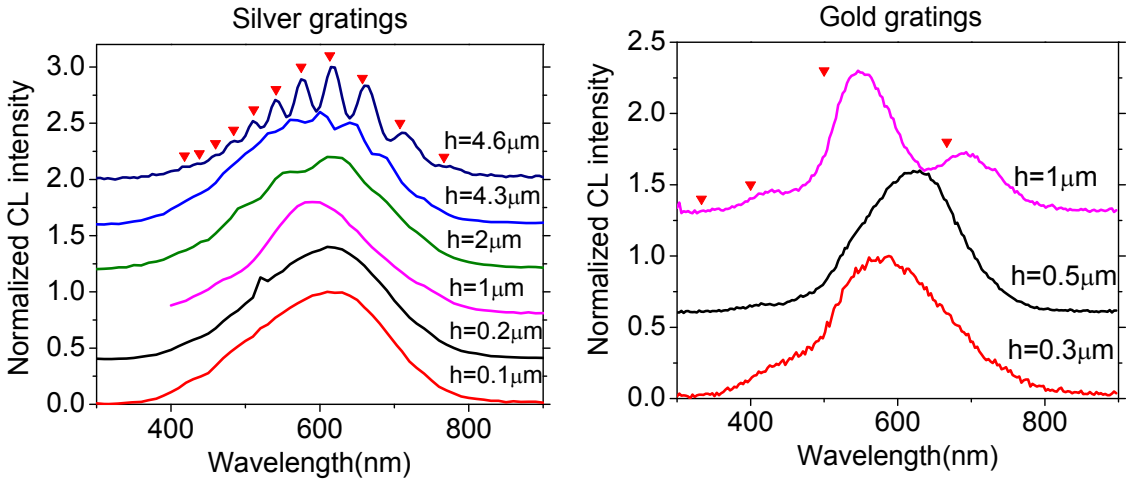


Fig 2. (left) CL spectra for 20-micron-period Ag gratings, and (right) for 7.5-micron-period Au gratings, of different amplitudes, with grating bars perpendicular to the optical collection axis. A flat featureless baseline amounting to about 10% of the peak signal has been subtracted. Then the data were normalized to the peak and given successive 0.4 and 0.6 vertical offsets for silver and gold samples, respectively, for clarity. Triangle symbols indicate resonance positions according to $\lambda = 2h/m$, m = integer.

Fig. 3 (left) presents a plot of the modulation peak separation vs. wavelength for both Au and Ag gratings. The modulation period increases with increasing wavelength and with decreasing grating amplitude. Fig. 3 (right) presents the peak positions vs. the resonance order m. In cases of weak modulation, peak positions were determined from the deriviative of the CL spectra. The data fit well to the curves $\lambda = 2h/m$, m = integer.

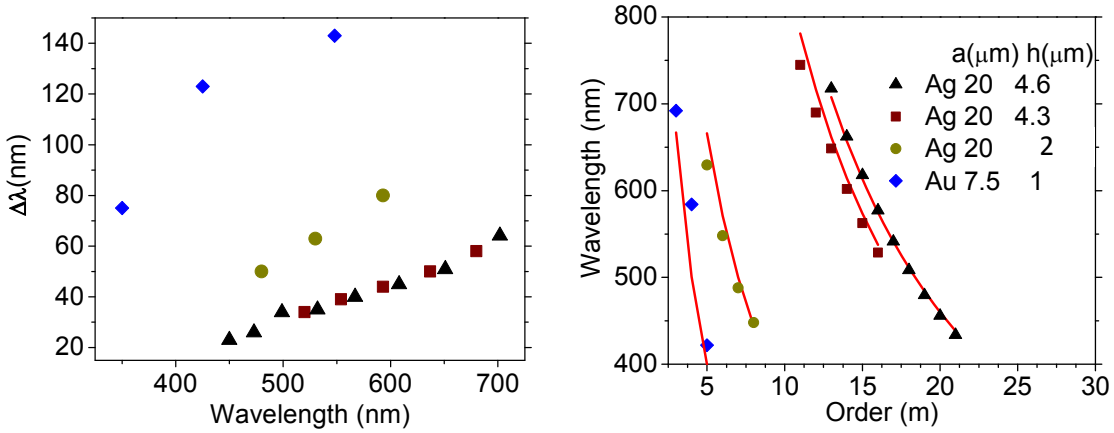


Fig 3: (left) Separation of modulation peaks as a function of wavelength. (Right) Modulation peak wavelength vs resonance order. In the right graph symbols are data and curves are calculated according to $m\lambda = 2h$.

Fig. 4 (left) presents the raw CL spectra for different distances Z below the mirror of the 20-micron-period 4.3-micron-amplitude silver grating. The signal is maximum for the closest distance, namely with the grating in the focal plane of the parabolic mirror, for both parallel and perpendicular orientation. At this position, the CL intensity is more intense for parallel orientation than for perpendicular. The visibility of the modulation increases with Z. The modulation peaks are blue shifted at the smallest Z value.

Fig. 4 (right) presents similar Z-dependence for the 7.5-micron-period 1-micron-amplitude gold grating. For parallel orientation, the intensity decreases monotonically with increasing Z. For perpendicular orientation the trend is similar but not monotonic for the intermediate distances. The modulation peaks are blue shifted at the smallest Z value. At the mirror focus, both orientations have similar intensity. There are too few modulation peaks to clearly quantify their visibility.

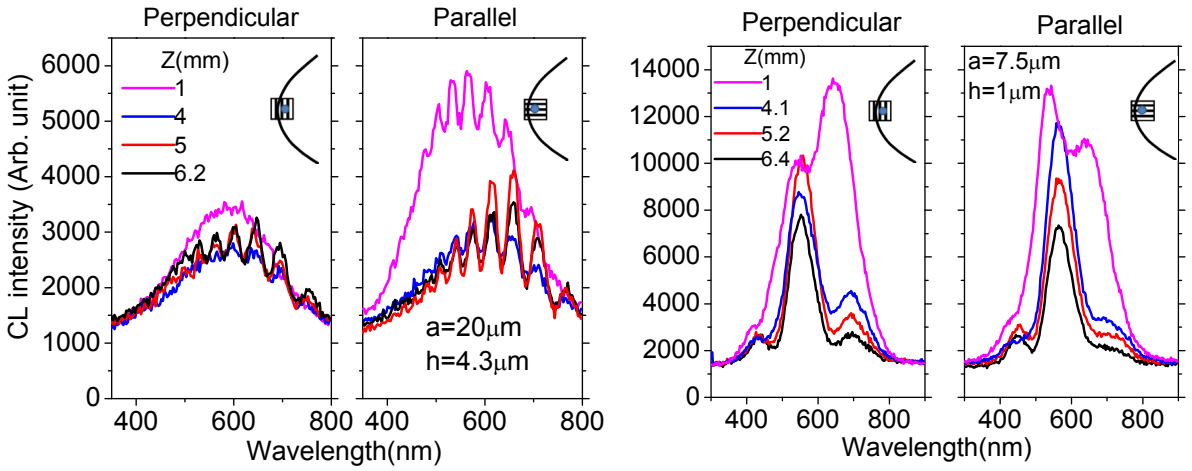


Fig 4: (Left) Raw CL spectra for 20-micron-period 4.3-micron-amplitude silver grating as a function of separation from collection parabaloid. (right) Same for 7.5-micron-period gold grating with 1μm grating amplitude. Both parallel and perpendicular orientations are presented.

Fig. 5 (left) compares the derivative of the CL spectrum for the 20-micron-period 4.6-micron-amplitude grating for parallel and perpendicular orientations. A phase shift in the modulation is observed. Fig. 5 (right) presents CL spectra for different electron beam energies of 20 and 30 keV. Apart from an upward shift of a few % for the 30 keV spectrum over the entire range, there is little change in the spectral shape or in the characteristics of the modulation. This observation argues against any explanation for the CL spectrum that depends on the electron velocity.

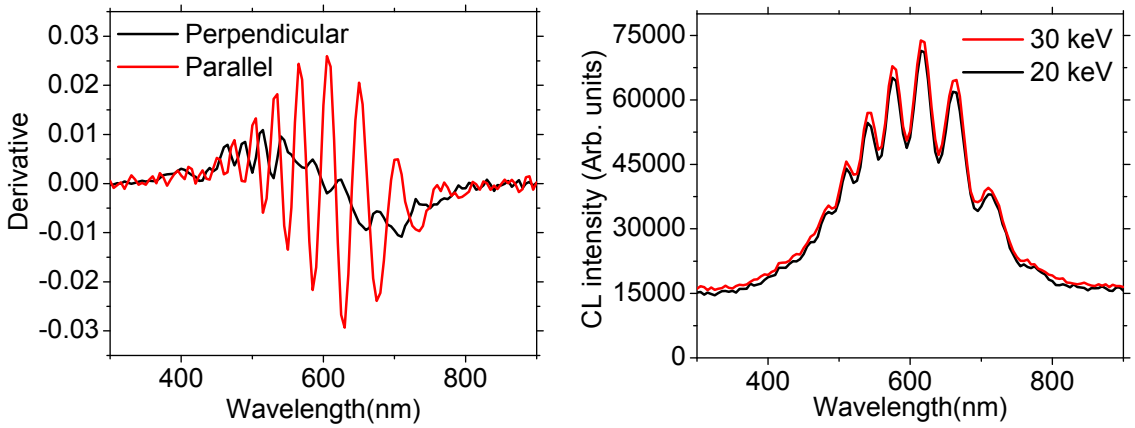


Fig 5. (left) Derivative of CL spectrum for 20-micron-period 4.6-micron amplitude Ag grating for perpendicular and parallel orientations. (right) Raw CL spectrum for 20-micron-period 4.6-micron-amplitude grating for 20 and 30 keV electron energies.

Fig. 6 presents CL spectra for a second 20-micron-period Ag grating sample with amplitude 4.6 microns, which was nominally identical to the first, for different areas rastered over by the electron beam. For each grating orientation, there are three curves corresponding to rastering of the ~10 nm electron beam over of a single grating bar, a single grating valley, or 4-5 grating periods intercepts the 10 nm wide electron beam. All three situations give nearly identical spectra. The CL band is weaker, but the oscillations stronger when the grating lines are perpendicular to the collection axis. The modulation appears less deep than in Fig. 2, in part because the spectral resolution was worsened from 5 to 10 nm. If interference between light emitted from bars and trenches is to explain the observed modulation, it means that the actual instantaneous area of luminescence excitation must have a diameter greater than 20 microns. This is only conceivable if electron-beam induced current within the metal surface spreads the instantaneous excitation area far beyond the actual 10 nm electron-beam spot size. The estimated maximum dwell time for the rastering electron beam on a single 10 micron wide grating bar is ~20 μs, which is very much longer than typical ns time-scales for allowed electronic luminescing transitions.

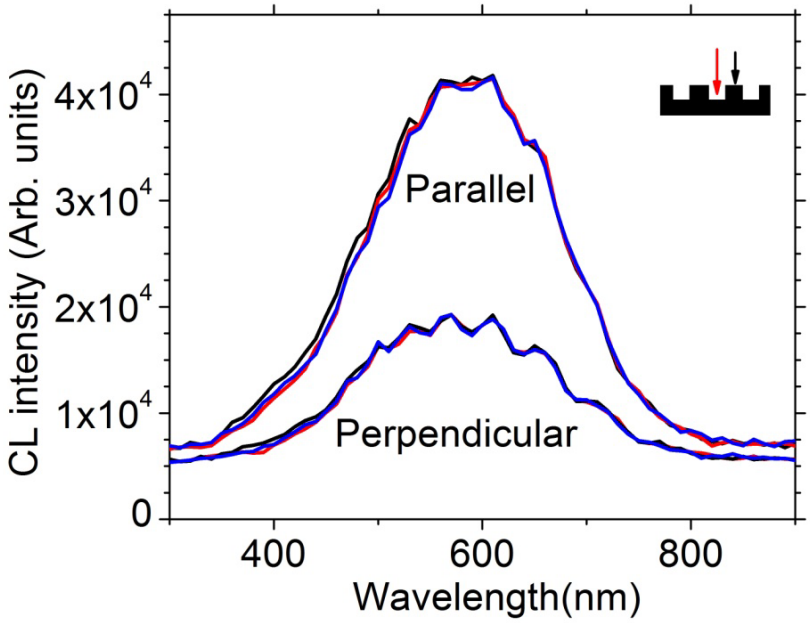


Fig 6: CL spectra of a 20-micron-period 4.6-micron-amplitude Ag grating. The inset schematic shows how the electron-beam rastered over a single grating bar or valley for two the three spectra for each orientation. The third spectrum corresponds to an area scan over 4-5 periods.

Fig. 7 (left pair) presents CL spectra when the e-beam is incident on smooth Ag just outside of the grating area to the "left" or "right", namely, with the grating shifted toward or away from the spectrometer, respectively. Fig. 7 (right pair) presents CL spectra when the e-beam is incident on smooth Ag just outside of the grating area on "top" or "bottom", namely, with the grating shifted laterally with respect to the collection axis. In comparison to spectra taken with the e-beam directly incident on the grating (e.g. Fig. 6), the intensity is about 10x less. For perpendicular orientation, there is practically no signal at all except when the electron beam is in the left position. For parallel orientation, the intensity for L is ~4x stronger than for R, or the nominally symmetric T and B positions, the T intensity is somewhat larger. There is little dependence on e-beam distance from the grating on 1 2 micron length scales.

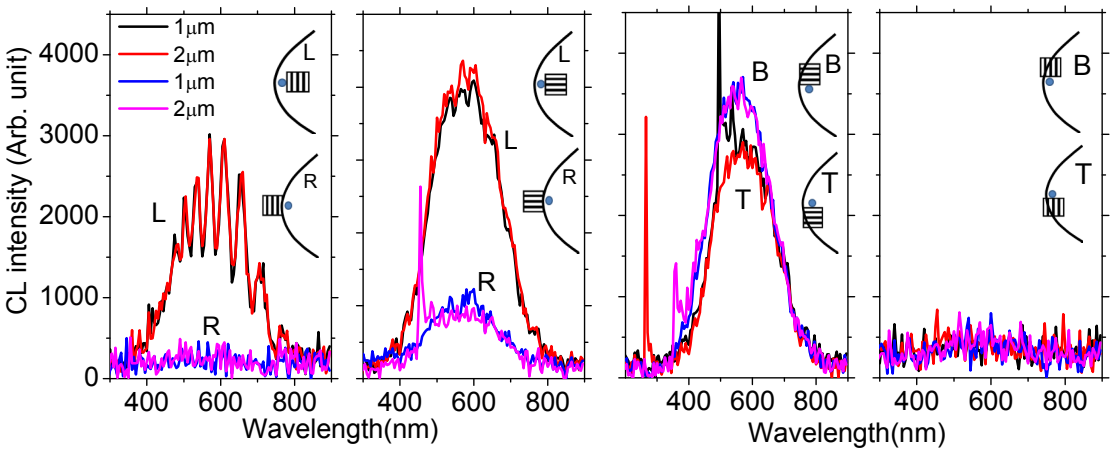


Fig. 7 (left pair) CL spectra for the 20-micron-period 4.6-micron-amplitude Ag grating when the electron-beam is incident to the left or right of the grating for (right) parallel and (left) perpendicular orientations. The distance from the edge of the grating is 1 or 2 microns as indicated. Fig 7 (right pair). CL spectra for the 20-micron-period 4.6-micron-amplitude Ag grating when the electron-beam is incident on the top or bottom sides of the grating for (right) parallel and (left) perpendicular orientations. The distance from the edge of the grating is 1 or 2 microns as indicated.

Fig. 8 presents CL spectra for a 20-micron-period 4.3-micron-amplitude Ag grating for two Z values and for a larger range of separations between electron beam and grating edge. Grating orientations and relative positions (L,R,T,B) are indicated. As before, the strongest signal occurs when the grating surface is at the focus of the parabaloid, and here the visibility of modulation peaks is the smallest. The intensity and modulation is independent of e-beam distance from the grating edge for distances of up to at least 10 microns. The background spectrum corresponds to a position of the electron beam at least 1 mm from the grating on smooth Ag. This shows that the existence of the band we have been studying depends on the proximity of the electron beam to the grating. As was observed in Fig. 7 for parallel orientation, the T position gives weaker intensity than B, despite the evident symmetry.

## 3. DISCUSSION

An initial hypothesis for the origin of the periodic structure in the CL spectra is that there may be periodic variations with wavelength in the number of diffraction orders collected, due to the finite acceptance angle of the parabolic mirror. However, this cannot explain the observations since the number of orders collected decreases monotonically as wavelength increases. Moreover the number of orders collected in visible light for a 20-micron-period grating is so large, that a change in orders collected by unity would amount to only a few percent changes in intensity and thus could not explain the observed fringe visibility.

All the data suggest that the modulation is due to interference between CL emitted simultaneously by grating bars and valleys. The dwell time of the electron on any single bar or valley is of order 20 microseconds (or much longer depending on the raster direction). This time is much longer than any likely emission time scale, so that if light were excited only directly under the electron spot on a bar, that light would be gone before any light could be emitted by a valley, leaving no opportunity for interference at the detector. Instead, it appears that electron beam induced current must CL simultaneously from areas on the surface having dimensions large compared to the grating period, i.e. tens of microns in diameter. By “simultaneous” we mean with in ns time scales typical for allowed electronic transitions. This requires electron velocities in the metal of only ~$10^4$ m/s, which very reasonable in comparison to usual hot electron velocities.

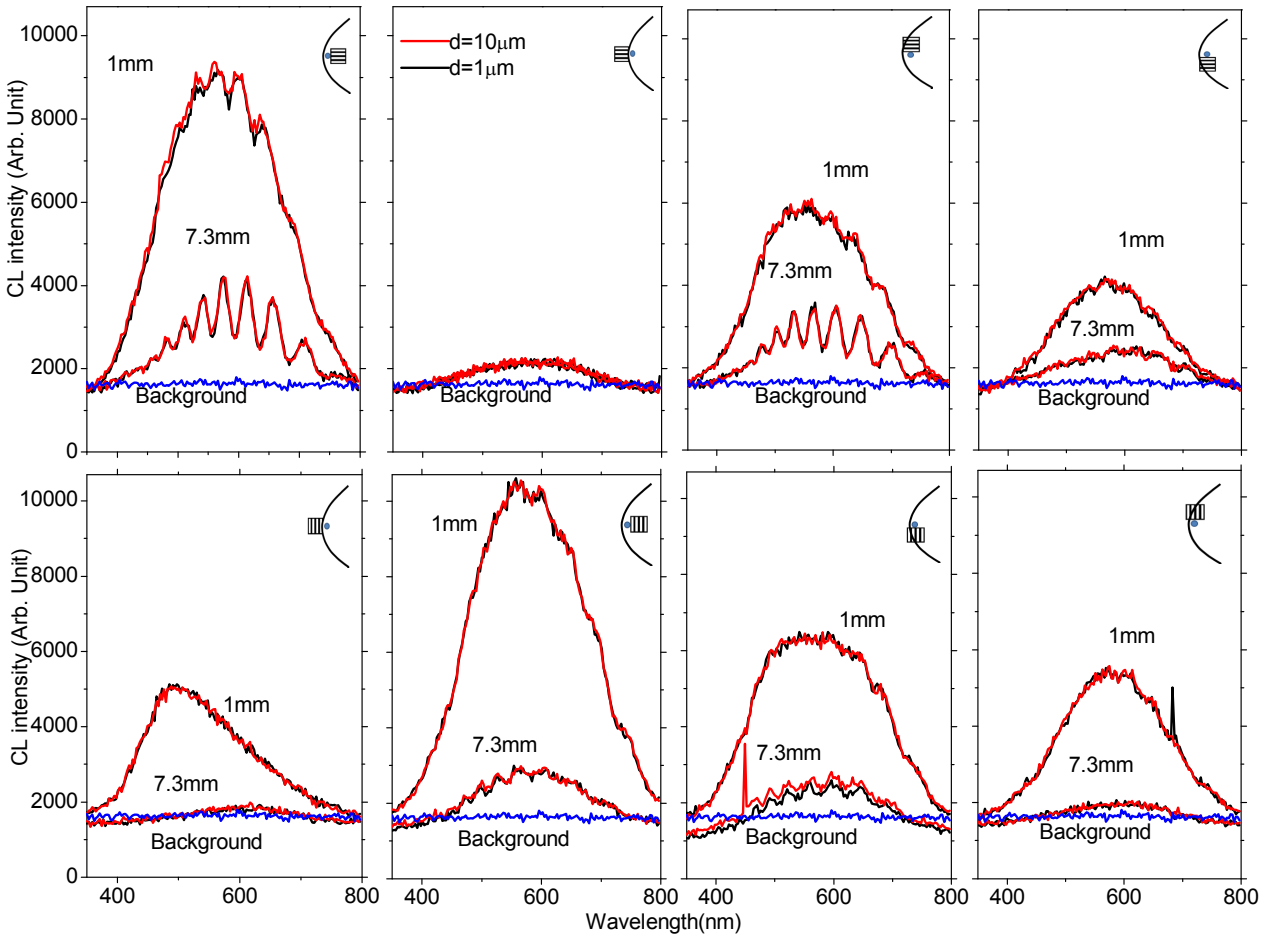


Fig. 8. CL for 20-micron-period silver gratings with 4.3 μm amplitude for Z = 1 and 7.3 mm, as indicated. Grating orientations and electron beam positions are indicated in the schematic insets. For each Z value there are two nearly indistinguishable curves, corresponding to distances of the electron beam from the grating of 1 and 10 microns, respectively. The flat data curves are background spectra obtained with the electron beam on smooth unstructured silver at least 1 mm from the gratings.

Fig. 9 explains the dependence of the fringe visibility on Z. When the grating is in the focus of the collection optic, rays are collected by the system only for a small spot on the surface. When the grating surface is below the focus, rays from a larger area on the sample are collected, allowing interference at the detector from a larger number of bars and valleys.

The origin of the CL signal itself needs also to be considered. Refs. [1,2] suggest surface contamination as one possible explanation for the bulk of the signal. The observation of interference fringes for CL emanating from bars and grooves simultaneously indicates that electron-beam induced current is able to excite CL from spots of several 10s of microns diameter simultaneously. Since surface contamination is likely to be in the form of non-conducting salts or oxides, our observations do not support this hypothesis.

Interband transitions involving the electronic structure of the metal were also suggested in[1, 2]. However, we observed no significant difference in the spectral envelop of the CL for Ag and Au samples. Since the electronic structure of Ag and Au are distinctly different, accounting for the yellow color of Au, our observations do not support this hypothesis for the origin of the signal.

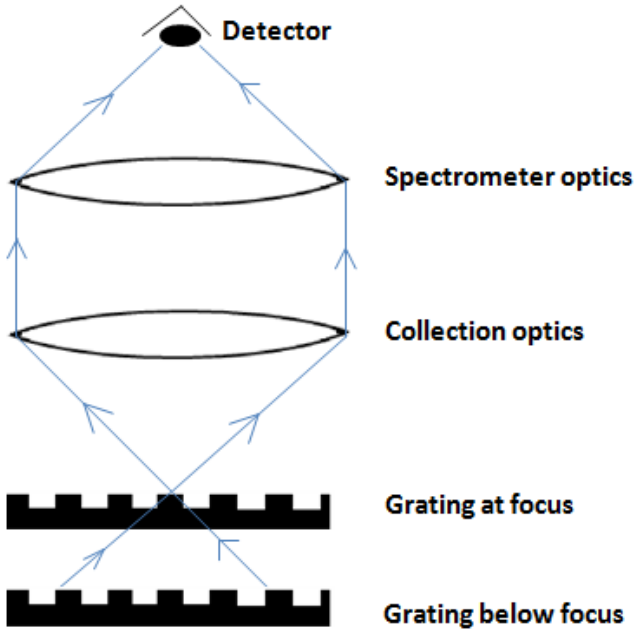


Fig 9: Schematic diagram of CL collection optics to explain the Z dependence of the spectral modulation visibility. Instead of parabolic mirror a lens is shown as the collection optics for ease of explanation. For grating at focus only emission from small region is collected. When the grating is below focus more periods contribute CL that can interfere at the detector.

A third suggestion was the collision of incident electrons with their image charges, which together form collapsing dipoles[1, 2]. Solution of Kepler's problem for the collapsing dipole shows that the incident electron deviates from uniform rectilinear motion only during the last mm of its travel to the surface, giving a characteristic time for the collision of only ~$10^{-11}$ seconds. This puts the peak of the collapsing dipole emission spectrum[10] at a frequency of 100 GHz, i.e. mm-waves. Thus the collapsing dipole explanation comes nowhere near explaining the observed CL spectrum.

The peak of inverse-photoelectron effect has been suggested. However its peak is expected to occur at wavelengths near 300 nm[7, 8]. Transition radiation is indicated as the most important source of the surface plasmons[6], which were the subject of study in Refs [1-4]. For silver, transition radiation peaks at ~350 nm wavelength[11, 12, 13]. In the spectral range of our experiment, transition radiation gives no peak.

Thus, none of the explanations so far proposed can explain the observed envelop of the CL emission spectrum. Our measurements show that the emission spectrum becomes flat and weak when the e-beam is on smooth metal far from the grating. This shows that the actual envelop of the CL observed has something to do with the grating itself.

## 4. SUMMARY

CL spectra were collected for Gold and Silver gratings with different grating periods and amplitudes. The CL spectra are characterized by a broad band in the wavelength range 400-800 nm. A strong quasi-periodic modulation appears in the band for gratings of sufficient amplitude, which can be explained as interference between radiations emitted simultaneously from grating ridges and troughs, though the electron beam bombards only a tiny area on one or the other at any instant. CL collected at different orientations and positions in the gratings indicate that the magnitude and shape of the spectrum depend strongly on proximity of the electron beam to the grating. Different mechanisms such as surface contamination, inter-band electronic transition, collapsing dipole and inverse photoelectron emission, which have been suggested as the origin of the spectra, in fact do not explain it.

## ACKWOLEDGEMENT

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