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Interference in edge-scattering from monocrystalline gold flakes [Invited]

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Historically, the field of plasmonics [1] has explored the interaction of light with the free electron gas, with a predominant attention to amorphous and polycrystalline noble metal nanostructures and thin films, [2] while less attention has been devoted to plasmons supported by monocrystalline materials. More recently, chemically synthesized monocrystalline gold flakes have been receiving increasing attention within the plasmonic community. In many aspects, such colloidal gold nanoparticles show superior plasmonic properties, as compared to evaporated polycrystalline films. [3–6] Atomic flatness and well-defined crystal structure offer larger plasmon propagation lengths and sharper resonances due to lower Ohmic losses and reduced surface scattering. [7] These favorable properties have been utilized in the design and fabrication of various plasmonic devices, such as nano-circuits, [3, 8] nano-antennas, [9–11] tapers, [12] and plasmon billiards. [13, 14] However, flat metal crystals are rarely true single crystals, but rather twins joined at pairs of stacking faults. [15] This is no coincidence, because the strong lateral growth involving {100}-facets requires the presence of at least 2 stacking faults within the seed. [6] These defects play an important role in the crystal growth [5] and might exhibit interesting plasmonic phenomena of electronic 2D states. This, along with the well defined material properties of single crystals, renders them excellent candidates for the observation of quantum effects, [16, 17] or of anisotropic nonlinear or nonlocal response e.g. due to the deviation of the Fermi surface from a perfect sphere. This is especially true for sub-micron particles, as quantum corrections to the classical electrodynamics manifest increasingly when approaching the subwavelength scale and reaching the atomic dimensions. [18, 19]

Differences between the material properties of mono- and polycrystalline metals are both important for applications as well as interesting in their own right. Moreover, the highly ordered
atomic structure of single crystals is also reflected in their geometry with very well defined angles, atomically flat surfaces and sharp edges. The quality of these features is well beyond what is currently achievable with state-of-the-art nano-patterning of polycrystalline films, [20] and they provide valuable material for the basic research of nanoplasmonics in finite-size metal geometries e.g. on the propagation of surface-plasmon polaritons (SPP) along the edges of gold crystals. [21,22] Several examples for such studies have been conducted for particles that are small compared to the wavelength of light. [23–26]

Crystal-related morphologic features are of course by no means restricted to subwavelength-sized particles, but also appear in fairly large objects such as the gold flakes studied in this paper with lateral dimensions greater than 10 µm and thicknesses around 1 µm. One such non-trivial feature is the fact that the sidewalls (for convenience referred to as "edges") of our nearly hexagonal flakes are asymmetrically tapered and that two types of such edge terminations alternate around the flake. As a result, each edge is dissimilar to both adjacent edges and the opposing one. This lack of symmetry with respect to mirroring and 180° rotation can be seen in high-resolution scanning-electron microscope (SEM) images (Fig. 1(a)-(c)). Yet quite often, this detail is ignored and the edges are simply approximated as rectangular truncations [21,22]. However, it reflects the fact that the face-centered cubic (FCC) gold lattice is symmetric with respect to neither a 180°-rotation nor a mirror operation about the [111]-axis. It is therefore a large-scale manifestation of the atomic order and can lead to a significant difference in the optical far-field properties as we show here.

In this work we report on a distinct difference in the scattering of visible light from the two types of edge terminations of colloidiy grown gold flakes with thicknesses around one micron. Even though in an optical bright-field (BF) our flake looks perfectly hexagonal (Fig. 1(d)) and seemingly exhibits six fold symmetry, difference in scattering appears as differently colored edges when observed in an optical dark-field (DF) microscope under lower numerical aperture (NA) collection conditions (see Fig. 1(e)-(h)). We conclude that this is the far-field manifestation
of the fact that opposing flake edges make different angles with the substrate, which in turn is a macroscopic consequence of the inherent chirality along the [111]-axis of the FCC lattice.

2. Results and discussion

We grew quasi-monocrystalline gold flakes on a silicon wafer substrates from chloroauric acid in the modified Brust–Schiffrin method [27] involving thermolysis of the precursor instead of chemical reduction (see Methods section for further details). This is known to yield flakes, which are large [28] and feature hexagonal, triangular and truncated triangular shapes with high aspect ratios up to 100. We obtain lateral sizes of up to 100 microns with thicknesses between several dozen nanometers and few microns. From the symmetries of the FCC gold lattice, one would expect the crystals to be bounded by facets of {111}- and {100}-types with threefold and fourfold symmetries, respectively. This is illustrated in Fig. 1(a)-(c), which show SEM images with artificial colorization indicating crystal planes of the corresponding facets. Therefore, it seems safe to assume the large top and bottom faces to be of {111}-type. [5] As a result, each of the three or six edges of the flakes is composed of one {111}- and one {100}-type facet, which meet at an angle of \( \approx 125.3^\circ \) and make angles \( \alpha = \arccos(1/\sqrt{3}) \approx 54.7^\circ \) and \( \beta = \arccos(1/3) \approx 70.5^\circ \) with the central plane, respectively. Consequently, the cross sections of the flakes consist of an upper and a lower trapezoids with different heights \( h_u \) and \( h_l \), but fixed angles, as illustrated in Fig. 2.

![Fig. 2. Schematic drawing of the flake's cross-section (cut through two opposite edges) with indicated geometrical parameters and Miller indices of the facets.](image)

The strong imbalance in the size of the top and bottom {111}-planes over all others is due to stacking faults (more precisely multiple twin planes), which form in the early stage of the crystal growth. Such defects commonly appear in the metals with FCC crystal structure, especially in gold, as they have some of the lowest defect energies [29]. They lead to quite different growth rates along different crystal axes and thus cause high aspect ratio of the crystals. Therefore, such thin flakes are not strictly speaking monocrystalline, as commonly referred to, but twins.

It is noteworthy that the FCC-lattice has only three-fold symmetry in the {111}-plane even though such a crystal facet might be perfectly hexagonal, as one shown in Fig. 1(d). This is the result of the chirality of the FCC-lattice along the [111]-axis, which is due to the existence of two different stacking patterns. Macroscopically, it manifests in the aforementioned two types of flake edges, which appear with threefold symmetry. In the following, we refer to edges where the side facet touching the substrate is of {111}-type or {100}-type as type-A or type-B edges, respectively. As it turns out, this three-fold symmetry and therefore the lattice chirality can be directly observed with an optical microscope.

We noticed that flakes which look almost perfectly hexagonal in the optical bright-field and high-NA dark-field (Fig. 1(d),(e)) exhibit very different scattering spectra from the two types of edges. This is visible to the naked eye under DF conditions and becomes more prominent
with decreasing collection NA, as shown in Fig. 1(f)-(h). Images were acquired using the same objective lens and the same illumination conditions (light from DF condenser impinging on the sample at a grazing angle $\gamma \approx 12^\circ$), and filtering the collected light in the Fourier plane, as described in details in the Methods section.

We find behavior that is qualitatively similar to that depicted here, yet with different shades of red, yellow and green commonly for flakes with thicknesses around 1 micron, so it appears to be a geometry-related effect. In order to further understand the underlying process, we first performed 2D finite-element calculations in p-polarization. This is sufficient for qualitative results, because we observed experimentally that with polarized illumination only the edges perpendicular to the incident polarization appear in dark-field and that the scattered light is p-polarized itself. We then post-processed the data with a far-field filtering procedure that mimics the effect of a low-NA objective (see Methods section for further details). Figure 3 shows experimental spectra acquired with NA $\approx 0.4$, which provides good contrast while keeping sufficiently strong signal, for two adjacent edges of the flake shown in Fig. 1. Alongside is shown a numerical spectrum calculated using nominal dimensions ($h_u = 130$ nm and $h_l = 580$ nm, as measured on the real flake), idealized illumination conditions and the permittivity of monocrystalline gold given by interpolated experimental data from Olmon [30]. Although we clearly do not obtain quantitative agreement, the experimental and numerical results show the same qualitative features: a peak for the type-A edge surrounded by troughs and a similar behavior for the type-B edge red-shifted by some 100 nm. We postpone the discussion of possible origins for this mismatch and first focus on the physical mechanism. However, we do emphasize at this point that the spectra of different flakes differ significantly in the positions of peaks and troughs, but always show the general features of an interference pattern.

Fig. 3. (a) Experimental and (b) simulated DF spectra of the two types of edges of the flake with nominal dimensions $h_u = 130$ nm and $h_l = 580$ nm. Both experimental and simulated spectra are acquired with NA $= 0.4$.

The physical origin of the different scattering spectra of the type-A and the type-B edges is the interference between a surface-plasmon wave and free-space propagation of light, which we concluded from a careful analysis of the numerical simulations, especially for varying values of the flake thickness parameters $h_u$ and $h_l$. We observe that light scattered directly into a low-NA objective stems predominantly from the upper facet (characterized by $h_u$), while the direct scattering from the lower facet is directed predominantly downwards, as one would expect from geometric optics or basic diffraction theory. Varying the parameter $h_u$ in our calculations caused broad-band changes to the scattering efficiency while leaving the beating period virtually
unchanged. The upper edge appears to act as an effective point-like dipole. This holds true in simulations even if $h_u \approx h_l$. In contrast, varying $h_l$ mainly changed the beating period and strongly shifted the peaks, so the resonances are linked to the length of the lower facet. Standing waves on that facet were considered, but did not match the observed beating period. As the illumination both in the experiment and the simulation is essentially at the Brewster angle for an air/silicon interface, light reflected from the substrate also does not enter the picture. Although the light scattered by the edge downwards hits the substrate at a different angle and might participate in the interference, we anticipate it as a weak effect.

This leads to the following explanation: the light emanating from the upper facet has two main contributions. Firstly, the scattered light is coming from direct illumination of the upper facet (blue arrow in Fig. 4(a)). However, there is also a second, indirect path illustrated by red arrows in Fig. 4. Like every metallic surface discontinuity, the lower corner of the crystal couples incident light to SPP. The resulting SPP travels up the facet, where it couples out to the far-field and contributes to the scattered radiation. Depending on the phase accumulated in this process, the direct and indirect radiation interfere constructively or destructively in the far-field, leading to a scattering spectrum that depends sensitively on $h_l$, the edge type, the grazing angle $\gamma$, the collection NA and the SPP dispersion relation. The in-coupling of the secondary path is significantly enhanced by the presence of a high-index substrate – with low-index substrates the effect is much less prominent, as we observed both experimentally and in simulations.

The phase difference between the direct and the indirect path is sketched in Fig. 4(b). The sample is illuminated by the DF objective under a grazing angle $\gamma \approx 12^\circ$, which means that the illumination light impinges the lower flake facet at an angle $\theta = \beta - \gamma$ or $\theta = \alpha - \gamma$ for type-A and type-B edges, respectively. As a result, the upper and the lower corners of the edge are excited with a phase difference $\Phi_1 = \exp(ik_0L \cos \theta)$, where $k_0$ is the vacuum wave number of the light and $L$ is the length of the facet, i.e. $L = h_l/\sin \beta$ or $L = h_l/\sin \alpha$ for type-A and type-B edges, respectively. Afterwards, the indirect path gains an additional phase $\Phi_2 = \exp(ik_{\text{SPP}}L)$ while traveling along the facet, where $k_{\text{SPP}}$ is the wave number of the SPP. Thus, the total phase difference between the direct and the indirect path (excluding other phase contributions from additional processes such as standing waves on the lower facet, nonzero SPP excitation phase at the lower corner and scattering phase at the upper facet that are different from the incident
wave’s phase) is
\[ \Delta \Phi = \exp[i(k_{\text{SPP}} + k_0 \cos \theta)L] \]  
(1)

and we expect that the scattering spectra of either edge type depend periodically on the parameter \( h_l \) with a periodicity of
\[ \Delta h_l^{(A)} = \frac{2\pi \sin \beta}{k_{\text{SPP}} + k_0 \cos(\gamma - \beta)} \]  
(2)

for the type-A edge and with \( \alpha \) instead of \( \beta \) for the type-B edge. Using the permittivity \( \varepsilon_{\text{Au}} = -16 + 1.1i \) for monocrystalline gold \([30]\) at a vacuum wavelength of \( \lambda_0 = 700 \) nm as an example, and assuming \( \gamma = 12^\circ \), we find:
\[ \Delta h_l^{(A)} \approx 420 \text{ nm} \quad \text{and} \quad \Delta h_l^{(B)} \approx 320 \text{ nm}. \]

This means that we expect the scattering intensity observed at type-A or type-B edges to exhibit interference oscillations with the periods of 420 nm or 320 nm, respectively, when \( h_l \) parameter is varied.

These values for the periodicity are to be compared to the numerically simulated spectra in the Fig. 5, where the upwards scattered power for both types of edges at a fixed wavelength (700 nm) is plotted as a function of the lower flake thickness \( h_l \) with all other parameters (e.g. \( \gamma, h_u \), etc.) kept as in Fig. 3. We observe distinct oscillations with a periodicity of \( \approx 340 \) nm for type-B edges, which is in good agreement with the simple interference model. The periodicity of the type-A spectra is slightly less consistent as the spectrum is not a pure sinusoid (distances between minima, maxima and turning points give different "periodicities"). Anyhow, the periodicity is greater than for type-B edges and we extract a value of \( \approx 380 \) nm. This is still in qualitative agreement with the interference model. We attribute the disparity to the existence of a second, weaker resonant effect, potentially a Fabry–Pérot-like standing wave on the lower facet. Yet, the main effect is clearly visible, especially since no alternative explanation predicts oscillations in the 300–400 nm range.

Fig. 5. Simulated scattering intensity at \( \lambda_0 = 700 \) nm for the two types of edges with \( h_u = 130 \) nm and range of \( h_l \) values. Estimated periodicity of the oscillations are \( \approx 380 \) nm for the type-A and \( \approx 340 \) nm for the type-B edge. The horizontal lines show the estimates for \( \Delta h_l^{(A)} \approx 420 \) nm and \( \Delta h_l^{(B)} \approx 320 \) nm, according to Eq. (2).
So far, we have not discussed the agreement between experimental and numerical spectra (Fig. 3). Both panels show qualitatively similar behavior. The most striking differences are an overall red-shift by some 100 nm of all features in the experimental spectrum and a significantly reduced amplitude towards the blue spectral range. This is partially due to simplifications and uncertainties in the numerical model. Firstly, in our simulations we choose a 2D finite-element model with plane-wave illumination impinging normally on the edge. In contrast, the illumination in our dark-field experiment is from a range of azimuthal angles covering a sector of $60^\circ$. We expect that non-normal incidence would lead to considerable red-shift of the interference effect. Secondly, also the angle of grazing illumination in the experiment is not well defined. Illumination light arrives at the edge from an indefinite range of grazing angles around approximately $12^\circ$. In the numerical model, we assume a plane wave from a grazing angle $\gamma = 12^\circ$. These two angular distributions lead to a smearing and potentially to a partial destruction of the interference pattern, especially at higher orders, i.e. shorter wavelength. Thirdly, we have conducted simulations with different common models for the permittivity of gold and found that variations in the plasmon dispersion relation can easily account for 50 nm shift in the spectral features, too. Finally, even though the flakes appear clean in the SEM micrographs, we suspect that the flake is covered by residue from the fabrication process, which again would lead to spectral red-shift and potentially to increased loss at shorter wavelengths.

The dependence of the observed edge color (and hence measured spectra) on the collection NA, which is clearly visible in Fig. 1(e)-(h), was also observed in the numerical simulations: interference peaks become wider and less prominent with the increasing value of NA in the above-mentioned post-processing filter. However, the effect is not as pronounced as in the experiment, presumably due to the idealized illumination conditions in the simulations. This behavior also fits well with the analytical model: directionality of the interferential scattering (that manifests in collection NA-dependent apparent edge colors) is expected due to quasi-specular reflection in the direct path, and it should become more prominent with the increasing distribution of the illumination angles.

Within the limits of these uncertainties, we are confident that we have identified the main origin for the thickness-dependent dissimilar scattering spectra from type-A and type-B edges in quasi-monocrystalline gold flakes.

3. Methods

In the following subsections experimental and numerical methods used in this work are described.

3.1. Sample preparation

Gold monocrystalline flakes were prepared using the modified Brust–Schiffrin [27] method for colloidal gold synthesis in a two-phase liquid-liquid system via thermolysis [28]. In this method, an aqueous solution of the chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) in concentration $0.5 \text{ g mol}^{-1}$ is used as the precursor. It is mixed with a solution of tetracetylammonium bromide (TOABr) in toluene in a vial and stirred using a magnetic stirrer for approximately 10 minutes at 5000 RPM. During this process $\text{AuCl}_4^-$ ions are transferred from aqueous solution to the toluene and TOABr acts as a phase transfer catalyst. After that the mixture is left in rest for approximately 10 minutes, during which two phases – aqueous and organic – separate. The substrate (n-type Si wafer) is prepared: a piece of silicon wafer is pre-cleaned using ultrasonic bath in acetone, isopropyl alcohol (IPA) and ultrapure water (Milli-Q). After drying with nitrogen gas the substrate is pre-baked on a hot plate at 200 °C for approximately 5 minutes for dehydration purposes. In the following step few microlitres of the organic phase are drop-casted onto a substrate which is then kept on the hot-plate at 160 °C for 30 minutes. After that the sample is cleaned in toluene at 75 °C temperature, acetone and IPA, which removes the greater part of the organic solvent. After the sample is dried with a mild nitrogen blow, a large number and variety of gold flakes are found on
the surface of the substrate.

### 3.2. Spectroscopy

DF spectroscopy measurements were performed using the Zeiss Observer microscope (Epiplan-Neofluar HD objective 50x, NA=0.80) and Andor Kymera 193i spectrograph equipped with Andor Newton CCD camera. Additionally, two lenses (achromatic doublets with focal lengths 15 and 20 cm) and an iris diaphragm were used to create the so-called 4f correlator system for spatial filtering (i.e. NA selection). For the measurements described in this work we have calibrated diaphragm opening to correspond to \( \text{NA} \approx 0.4 \). This value of the collection NA was chosen because it gives good contrast between two types of edges, while keeping sufficiently strong signal and high spatial resolution. Lenses with different focal lengths were chosen intentionally to obtain appropriate image magnification on the camera screen.

A standard tungsten-halogen lamp was used as an illumination unit in this setup. In order to achieve "one-sided" illumination, the DF mirror cube was modified to restrict the range of azimuthal angles of incidence, i.e. DF illumination ring was partially covered with an opaque sheet and only a sector of \( \approx 60^\circ \) was left open. Reported spectra were normalized to a reference spectrum, obtained by illuminating a white scatterer in the same conditions.

Additionally, a linear polarizer and analyzer were used to select appropriate polarization of the illumination and detected light (i.e. p-polarization for the specified edge of the flake).

In order to avoid any systematic error due to the experimental setup, we measured different edges by rotating the sample while keeping fixed all other settings.

### 3.3. Numerical simulations

Numerical simulations were performed in the frequency domain using a commercially available finite-element method (FEM) solver (Comsol Multiphysics 5.3). The geometry of the model is two-dimensional, implying homogeneity along \( z \)-axis direction (axis orthogonal to the plane of the flake’s cross-section). We consider this simplification to be appropriate as lateral dimensions of the flake are much larger than the thickness (i.e. \( w_l \gg h_u + h_l \)). The model assumes a plane wave with wavelength \( \lambda_0 \) at a grazing angle \( \gamma \). In the first step, the model solves for the electric field distribution in the vicinity of the air/silicon interface. For the refractive index of Si, we used interpolated experimental data by Aspens [31]. In the second step, a gold particle is placed on the substrate with the shape shown in Fig. 2 and fields calculated in the first step are used as a background source to obtain the scattered fields. The refractive index of monocrystalline gold is described by interpolated experimental data from Olmon [30]. The model uses triangular meshing (5 nm maximum element size in the metal domain, 8 nm in silicon) and fourth order polynomial basis functions. We have performed mesh refinement study, from which we assess second order convergence and estimate relative error in the reported numerical data to be less than one percent.

In the subsequent step, the simulated fields were post processed using a dedicated filtering method, which mimics operation of the microscope objective, i.e. selects only traveling waves which propagate within a given NA.

### 4. Conclusions

To summarize, in this work we have exemplified that the differences in the scattering spectra of the adjacent edges of the gold monocrystalline flakes, which we have first observed experimentally in the DF microscope, are far-field manifestation of the subwavelength-scale morphological features. We have developed a numerical model and filtering method which allows to simulate the experimental conditions fairly accurately. Through a careful analysis of numerical simulations, we have found that the height of the lower trapezoid in the cross-section of the flake (\( h_l \)) is the main parameter for determination of the scattering spectrum. Guided by analysis of numerical
results, we have developed an analytical model where the physical mechanism, which gives the main contribution to the observed scattering spectrum, is the interference between a surface plasmon in the lower facet of the flake’s edge and free space waves. The difference in the lengths of the facets of adjacent and opposite edges explains the difference in scattering spectra of those.

Finally, we speculate that the strong sensitivity to the plasmon dispersion relation in the described effect offers a possibility to estimate permittivity function of the monocrystalline gold flakes, provided they are known to be clean. Given that the flakes have well-determined geometries, and with possibilities for high resolution measurement of the length scales, simulations can be matched with the experimental spectra using permittivity as the fitting parameter. However, we emphasize that perfect matching can only be achieved with virtually plane wave-like illumination, which implies substantially improved control over the sample illumination e.g. by using a goniometer.

Author contributions

S. B. contributed to materials synthesis, sample fabrication, structural characterization, optical measurements, and simulations. J. L. contributed to materials synthesis and structural characterization. C. W. contributed the theory, modeling, and simulations. Y.Y. contributed to materials synthesis. F. T. contributed to optical microscopy and measurements. A. S. R. contributed to the optical microscopy and structural characterization. B. H. introduced materials synthesis and initial materials. The project was supervised by C. W., S. I. B, and N. A. M. All authors participated in the interpretation of results and the writing of the manuscript.

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