Surface plasmons are associated with enhanced and localized electromagnetic fields that are of interest for sensing (e.g., biosensors), light harvesting (e.g., solar cells), guidance (e.g., directional emission), nanoantennas or manipulation of incident light (e.g., color filters). Evolving from this, structural colors beyond the diffraction limit were recently developed. These structural colors arise from the interaction of light with nanostructured surfaces. Compared with chemical colors, structural colors do not bleach and are spectrally tunable. The recent progress in nanofabrication techniques allowed researchers to fabricate and study different color rendering plasmonic structures based on Au/Ag and Al nanodisks, Al nanopatches and metal–insulator–metal nanoresonators. These structures create polarization-dependent effects and a palette of colors mostly at normal incidence. While some applications require that the optical effects are angle-independent, others desire strong color rendering only for predefined observation directions. Here, we demonstrate a strong symmetry broken color rendering effect, for which a plasmonic sample generates colors only when viewed from one side of the surface normal.

To date, most of the color rendering substrates have been fabricated using gold or silver, mostly because of their high plasma frequency and low losses, but the high cost of these noble metals hinders the broad integration into practical applications. Aluminum, on the other hand, is the most abundant metal in the Earth's crust, and it finds a wide range of practical applications. It is cost-effective and stable due to the formation of a self-protective oxide layer. The plasma frequency of aluminum is even higher than the one of gold and silver, and its low losses in the ultraviolet (UV) and near-UV regime, combined with its low cost and ease in handling, makes it a very attractive candidate for plasmonic applications. Although structural colors based on aluminum have been shown recently, the practical and scalable fabrication of color rendering substrates has sparsely been demonstrated.

We develop a color rendering substrate composed of an array of tilted aluminum nanowires that possess a broken symmetry with respect to the surface normal.

ABSTRACT We fabricate and characterize large-area plasmonic substrates that feature asymmetric periodic nanostructures made of aluminum. Strong coupling between localized and propagating plasmon resonances leads to characteristic Fano line shapes with tunable spectral positions and widths. Distinctive colors spanning the entire visible spectrum are generated by tuning the system parameters, such as the period and the length of the aluminum structures. Moreover, the asymmetry of the aluminum structures gives rise to a strong symmetry broken color rendering effect, for which colors are observed only from one side of the surface normal. Using a combination of immersed laser interference lithography and nanoimprint lithography, our color rendering structures can be fabricated on areas many inches in size. We foresee applications in anticounterfeiting, photovoltaics, sensing, displays, and optical security.

KEYWORDS: symmetry breaking, angle-dependent, plasmonics, immersed laser interference lithography, Fano line shape, structural colors, aluminum
substrate. Because of the broken symmetry, the substrate exhibits strong color rendering only in one tilt direction, that is, the substrate looks colorful from one angle of observation whereas it appears colorless from the opposite angle of observation. This distinctive asymmetry originates from the angle-dependence of surface plasmon excitation coupled with the tilted geometry of the nanowires. We show that the interaction of surface plasmons with propagating modes gives rise to distinct spectral resonances, similar to extraordinary transmission or perfectly absorbing structures.\textsuperscript{12,23} We obtain a wide range of the RGB color spectrum by fine-tuning the fabrication steps. The symmetry breaking, color rendering substrates can be fabricated on a large scale, with high throughput and at low cost.

RESULTS AND DISCUSSION

Fabrication of aluminum plasmonic nanostructures in an up-scalable and cost-effective manner is a key element for sophisticated realization of applications based on plasmonics. In the following a detailed description of the proposed large-scale fabrication method is provided. Further the concept of structural colors permitting angular symmetry breaking effect based on this kind of structures is shown. After insights of the physical effects, a concrete realization of the optical effect is provided.

Fabrication Method. The proposed fabrication method is compatible with standard industrial roll-to-roll process\textsuperscript{24} and is illustrated in Figure 1. It involves immersed laser interference lithography for the fabrication of periodic nanoscale pattern. These patterns are subsequently used as a template for nanoimprint lithography. Evaporation with aluminum from an oblique angle generates asymmetric plasmonic structures and subsequent embedding with a polymer provides protection and enables the use at ambient conditions. Most of the nanofabrication techniques used in today’s research laboratories are either slow or very expensive (e.g., serial fabrication methods such as ion beam or e-beam lithography\textsuperscript{25,26} for master fabrication or immersed lithography for reproduction in chip technology\textsuperscript{27}). Moreover these techniques are often limited to a small area ($\sim$100 x 100 $\mu$m$^2$)$^{9,10,12}$ or require stitching techniques of the master structure to obtain large-area coverage. Laser interference lithography, on the other hand, is a parallel technique that can cover several square cm’s.\textsuperscript{28} Additionally, the depth and duty cycle of the periodic nanostructures can be tuned during the fabrication process. Unfortunately the fabrication of nanostructures with periods below $\sim$250 nm\textsuperscript{29} often requires the use of ultraviolet (UV) lasers (<400 nm) and optics, which are more expensive and difficult to handle. To be in-line with up-scalable and large-scale industrial fabrication methods, we use immersed laser interference lithography\textsuperscript{30} (Figure 1a) in which a prism (equilateral) with high refractive index is placed onto the photoresist covered by an index matching immersion liquid. This technique not only reduces the wavelength by the index of refraction $n_{\text{prism}}$, but it also increases the angle of incidence due to refraction at the prism surfaces (see Figure 1a). Therefore, the period $p$ of the pattern caused by the interference of the two beams can be reduced by a factor $\sim$2 compared to conventional laser interference lithography,\textsuperscript{21,30} e.g., $p \sim 160$ nm with a 441.6 nm laser. Exposure of the negative photoresist with subsequent development gives rise to a sinusoidal pattern with period $p$. Transfer of the periodic pattern into glass is achieved via angle evaporation of chromium (as etching stop layer) onto the photoresist and subsequent

![Fabrication Method](image_url)
etching into photoresist and borosilicate glass (Figure 1b–d). By tuning the process parameters, the period, depth, shape (rectangular or trapezoidal) and duty cycle (ratio of width of the ridge to period) of the resulting nanostructures can be tailored. To further enhance the sustainability of the template a replication in nickel can be fabricated through a galvanic process. Following the fabrication of a master by immersed laser interference lithography we use nanoimprint lithography\textsuperscript{21,24,31,32} to replicate the periodic nanostructures into a UV curable polymer, see Figure 1e. After replication, aluminum is evaporated from a well-defined angle $\alpha$ onto the replicated nanostructures (Figure 1f) via an electron beam physical vapor deposition process. Hereby the outer layer of aluminum forms a self-protective oxide layer of around 2–3 nm.\textsuperscript{33} Simulations show that this oxide layer has a diminishing effect on the optical properties but can lead to a slight red-shift. Finally, the samples are embedded in UV curable polymer (Figure 1g) to protect the aluminum nanowires against abrasion caused by ambient use. Figure 1h shows a scanning electron microscope (SEM) image of a fabricated sample prior to embedding. The transmission spectra of the samples were measured on a rotation stage with a photospectrometer. Figure 1i shows the transmission of TM-polarized light incident at an angle of $-60^\circ < \theta < 60^\circ$ (in air) with respect to the surface normal. Negative angles are those that are in the same direction as the metal evaporation.

**Geometrical Influence on the Optical Effect.** The evaporation of aluminum from an inclined angle leads to deposition at the slope and the top of the underlying nanostructures, which results in a symmetry broken geometry and gives rise to an optical anisotropy. This subwavelength lamella-like structure has the unique property of being indiscernible among certain angles, directions, respectively. This can not be achieved with in-plane, flat or even bulky structures, showing, e.g., directional emission,\textsuperscript{34} coupler\textsuperscript{35} or light scattering.\textsuperscript{36} Moreover, its asymmetric tilt geometry shows not only angle- but also direction-dependent excitation efficiencies. The theoretical effect of structural asymmetry has been reported in the literature,\textsuperscript{37} whereas mainly variation of the structure and not change of measurement conditions, such as the incident angle, led to a shift of the resonance. Moreover fabrication of such structures would be very challenging. The asymmetrical geometry can also be exploited for enhancing nonlinear effects, such as sum-frequency or second-harmonic generation.\textsuperscript{38,39} To optimize the transmission asymmetry we have performed a detailed study of the system parameters. The aluminum layer has been varied in the range of 5–30 nm to ensure high transmission values, while the period has been fixed at 197 nm to minimize diffraction effects in the visible range. We have also varied the evaporation angle, defining the ratio and area of aluminum deposited on the side and the top of the underlying nanostructures. Other parameters are the depth, duty cycle and slope angle of the nanostructures, which can be defined during the fabrication process.

**Angle-Dependent Transmission Indicating Strong Coupling.** Figure 2 shows transmission spectra of a plasmonic
substrate with a certain geometry (will be discussed later) excited by TM-polarized light under different incident angles $\theta$. Experimental measurements are compared with simulations done with the rigorous coupled-wave analysis (RCWA). For negative angles a pronounced spectral feature is observed, whereas for positive angles the transmission remains relatively flat. The pronounced spectral features observed at negative angles are the result of two optical effects, the Wood–Rayleigh anomaly (WR) and a localized surface plasmon resonance (LSPR). The Wood–Rayleigh anomaly (bold line Figure 2) is a spectral signature of a propagating resonance (PR) in a periodic nanostructure and refers to the disappearance of higher-order propagating modes at the wavelength $\lambda_{\text{R}} = p \sin(\theta) + n_{\text{surr}}$, where $p$ is the period of the structures, $n_{\text{surr}}$ the refractive index of the homogeneous surrounding medium and $\theta$ the angle of incidence in air. While the angle-dependent excitation of a PR gives rise to enhanced transmission, the excitation of a LSPR leads to a transmission dip. The LSPR depends sensitively on the geometry; the efficiency of excitation is strongly angle-dependent but not the spectral position. At high negative tilt angles strong coupling between the PR and the broad resonant LSPR results in a narrow and dispersive feature characterized by an asymmetric Fano-like line shape. We refer the resonance induced by the coupled mode as propagating plasmon resonance (PPR). In Figure S1, the transmission is calculated as a function of the wavelength and period of the nanostructures. As a signature of strong coupling we observe anticrossing of the two resonances. As an intrinsic property of the plasmon resonance, the PPR is excited by TM-polarized light arising only for angles $\theta < -30^\circ$.

**Polarization and Rotation Dependent Angular Transmission.**

For further characterization the influence of the polarization and the tilt angle on the optical properties are studied. Figure 3 shows the angular transmission spectra of the sample from Figure 2 upon TM-polarized (Figure 3a,b), TE-polarized (Figure 3c,d) and unpolarized light (Figure 3e,f) among the tilt angle $\theta$ and $\varphi$ of the sample. Tilting the sample perpendicular to the lines of the nanostructures is indicated by the angle $\theta$, whereas the angle $\varphi$ describes a tilt along the periodic nanostructures. As before described the plasmons are excited for TM-polarized light for a tilted incidence $\theta$ perpendicular to the periodic nanostructures (Figure 3a). In Figure 3c, upon TE-polarized light the aluminum nanolamellas show transmission spectra with a maximum following the Wood anomaly, which confirms that no surface plasmons are excited in the nanolamellas. On the other hand tilting the sample along the nanostructures, angle $\varphi$, does not show strong optical features. TM-polarized (Figure 3b) light shows a broadband response of the aluminum nanowires with a slight angle-dependency. Similar for TE-polarized light where a high transmission is observed (Figure 3d). More importantly, for usage in ambient conditions the proposed optical effect also has to be visible in unpolarized light. Figure 3e,f show clearly that the main optical feature, the distinct signature of the plasmons with its asymmetric angle-dependent feature, is so dominant in TM-polarized light that it clearly appears also for unpolarized light. This strong angle-induced asymmetry leads to the appearance of a color effect only in one of the four directions even in unpolarized light. An equivalent angle-dependent behavior for the excitation of plasmonic structures has been studied in symmetric systems.

**Near-Field Intensity Distribution.**

To further investigate the physical nature of the PPR we performed electromagnetic field simulations using the surface integral equation method (SIE). This computational method provides high accuracy in the near-field and is especially advantageous for open boundary conditions. Figure 4 shows the calculated fields for an angle of incidence of $\theta = -60^\circ$. The transmission spectrum shown in Figure 4a features a peak of high transmission that is caused by the interference of the incident light with the zeroth and first order diffracted fields. These fields are of nearly equal intensity and mainly show near-field enhancement between nanowires, see figure 4b. The transmission drops for longer wavelengths and reaches a minimum at $\lambda_{\text{R}} = 562$ nm. The strong decrease in transmission is caused by the
excitation of LSPRs of individual nanowires, which is associated with strong near-field enhancement at the tips and between the nanowires (Figure 4d) leading to an increased in-plane absorption. For even higher wavelengths LSPRs are no longer efficiently excited and the transmission increases again. The field enhancement decreases between the nanowires and at the tips from $\sim 4\times$ to $\sim 1.3\times$ and $\sim 72\times$ to $\sim 61\times$ respectively (Figure 4b).

Geometrical Influence on the Resonance. The spectral position of the PPR (at a given angle) is determined by the geometry of the plasmonic nanostructure (length, tilt and shape) and the duty cycle and period of the underlying nanostructures. The calculated transmission spectrum for varying period and varying length is shown in Figure 5a and 5b, respectively. In Figure 5a the length of the nanowires (126 nm) is fixed, whereas in Figure 5b we keep the period (197 nm) constant, each at an angle of incidence of $\theta = -60^\circ$. Regions of low transmission (blue areas) are associated with high absorption or in-plane propagation due to LSPR excitation (up to $\sim 95\%$). With this spectral tune-ability of the PPR the complete visible color range can be represented. In particular change of the period shifts the color effect, whereas modification of the length influences the spectral shape and contrast of the color. The length of the nanowires can be easily tuned via the evaporation angle of the metal. The additional evaporation on top of the nanostructures leads to a slight color appearance mainly at normal incident, but can be controlled with the duty cycle of the nanostructures. Figure 5c–e show comparisons of theory and experiment for different geometries (length of 74, 126, and 137 nm, width about 15 nm). The agreement between theory and experiment is very good.

Figure 4. Calculated field distributions for an angle of incidence of $\theta = -60^\circ$ (in air). (a) Far-field transmission spectrum calculated (line) and measured (dots). (c) Near-field evaluated at the transmission peak ($\lambda_d = 483$ nm) showing no regions of high intensity. (d) On the other hand, strongly enhanced fields at the tips (up to $72\times$) and between the nanowires (up to $4\times$) are observed near the plasmon resonance ($\lambda_d = 562$ nm). (b) For wavelengths beyond the plasmon resonance ($\lambda_b = 675$ nm) strongly enhanced fields are only observed at the extremities of the metal structures.

Figure 5. Simulated transmission spectra as a function of (a) period and (b) length of the plasmonic structures. The angle of incidence is $\theta = -60^\circ$. The transmission is lowest where the absorption due to excitation of LSPRs is highest. (c–e) Comparison of theory and experiment for different geometries (length of 74, 126, and 137 nm, width about 15 nm). The agreement between theory and experiment is very good.
Large-Scale Realization of the Optical Effect. Figure 6b–d depicts the measured colors (converted with CIE 1931 color space) of the samples characterized in Figure 5c–e under different viewing angles θ and φ (see scheme in Figure 6a). All samples show a distinct color at negative angles whereas at positive angles color neutrality is observed. Because of the angle-dependence of the PPR an angular color shift is observed. Colors appear in yellow to red (at evaporation angle 20°, a), red to purple (at 30°, b) and blue to green (at 40°, c). At normal incidence, only weak colors are observed. The color almost does not change for different viewing angles φ. Figure 6e shows photographs of a glass substrate illuminated by unpolarized diffuse daylight. It contains 4 patches (2 cm × 2 cm) of the same periodic nanostructures. Evaporation of aluminum onto different photoresist masks allows patterning the substrate in distinct colors by changing the evaporation angle and direction. The pattern was chosen such that each patch contains one animal utilizing structural colors in nature: a *morpho* butterfly (evaporation angle 30° top, 40° bottom), a *chameleon* (40°), a *damselfish* (20° top, 30° bottom) and a *hummingbird* (40°). The background of the animals was evaporated at an angle of 40° from the other direction. Furthermore, the wings and outline of the *hummingbird* and *morpho* butterfly respectively were evaporated (30 nm) onto the glass substrate before replication of the periodic nanostructures; they appear as shiny, nontransparent areas. At negative angles the animals appear in the colors yellow, pink and blue/green, depending on the tilt angle. The background appears in blue and green at steep angles but in the opposite direction. This color switching increases the appearance of the color and enhances attractiveness of the device. The color inhomogeneity of the structures fabricated at the same evaporation angle is mostly caused by the angular spread of the image for the observer. Additionally, the finite distance to the evaporation source leads to slight variation along the sample. This can be improved with a more distant source, which would be straightforward in roll-to-roll fabrication. At normal incidence a slight color appears which is mainly caused by the non-resonant polarization appearing blueish. This on the other hand can help to increase visibility of the colors at higher angles, since generally in unpolarized light the contrast of the plasmonic color decreases. For a more visible representation of the obtained colors, Figure 7 shows a CIE color plot (CIE 1931, xY color space) containing the samples of Figure 6b–d. The white triangle displays the standard RGB color range.

Besides changing the evaporation angle, the colors can be varied by the period, the nanostructures profile...
which lead to different geometrical shape of the aluminum nanolamellas (see Figure 5) or by the orientation of the underlying structures or lamellas. These enable practical large-scale fabrication of complex angular variable color images. While intense colors are obtained at negative angles, the colors at normal incidence are faint. They can, however, be enhanced by a larger duty cycle. A complex master structure containing pixels of such different nanostructures can enable fabrication of an optically very complex and appealing structure fabricated at only one fixed evaporation angle.

The asymmetrical color rendering effect fabricated and analyzed in this work has attractive applications in visual authentication allowing securing documents and goods, so-called optical security. Besides this specific studied geometry, perfect oblique metallic nanolamellas as well as nanolamellas with minor geometrical variations can be tuned to generate such highly asymmetric optical behavior. Moreover, it can be used for passive color filtering, in display technologies, VCSELs, light scattering and anticontrol. For larger periods we obtain a relative narrow resonance dip (fwhm $\sim 30$ nm) that is accompanied by strong intensity changes ($\sim 5$–80% with TM-polarized light) in the visible spectrum. Our simulations show a large figure of merit, which is of interest for refractive index change-based sensing applications. Furthermore, the strong absorption of light in the plane of the nanolamellas, can find use in thin-film photovoltaics. The active material would need to be placed between the nanowires where absorption is highest.

In contrast to diffractive gratings (such as blazed gratings) where the obtained color is solely governed by the grating equation, the proposed effect is based on zero order transmission. Zero order effects do not require a certain viewing angle or change rapidly with the illumination angle: this enables clear visibility in diffuse daylight or poor light conditions, which is often not possible with higher order optical effects. Furthermore, transmission or reflection efficiencies can be higher, since light does not dissipate into higher diffraction orders. Specifically in this case the efficiency and the plasmon excitation can be accurately controlled. This leads to a strong suppression of the optical effect in one tilt direction, which would be very challenging to achieve with diffractive gratings.

CONCLUSION

In summary, we have demonstrated symmetry-breaking structural colors based on tilted aluminum plasmonic nanowires. High transmission $\sim 80\%$ and high absorption $\sim 90\%$ is observed in selected frequency ranges, leading to strong color rendering even for unpolarized light. Immersed laser interference lithography allows us to fabricate periodic subwavelength features on a large-scale and enables tunability of the geometrical parameters during the fabrication process. Symmetry breaking colors are generated by evaporating aluminum from oblique angles onto the fabricated nanostructures, leading to tilted nanowires. This asymmetric geometry allows plasmon resonances to be excited by light incident from one side only. Strong and narrow absorption bands are generated by strong coupling between propagating resonances and plasmon resonances, giving rise to characteristic Fano line shapes. The strength of the coupling depends on the angle of incidence and the spectral positions of the individual resonances. While the period affects mainly the propagating resonance, the length of the aluminum nanolamellas defines the plasmon resonance. The resulting Fano dip can be tuned over the complete visible spectrum, giving rise to distinctive structural colors that range from red over green to blue and depend on the observation angle. Other material such as silver, gold or copper could be used to generate an equivalent effect at larger wavelengths (such as near-infrared and beyond).

EXPERIMENTAL SECTION

Fabrication. Immersed laser interference lithography was done with a HeCd laser (441.6 nm) on a damped table. A prism $n_{\text{liquid}} = 1.59$ at $435.8 \text{ nm}$, from Cargille, BK7 immersion liquid). The final device shown in Figure 6 was made by 4-fold replication (each square) of the master structure. Subsequently a protecting photoresist was exposed through distinct photomasks to evaporate aluminum at different angles ($20^\circ$, $30^\circ$ and $40^\circ$) and directions for the different pattern. The photographs were done in unpolarized light in front of a cloudy sky.

Characterization. The angle-dependent measurements were done with a PerkinElmer spectrometer (Lambda 9). Zero order transmission was directly measured with and without a Glenn-Thomson polarizer between the sample and the light source. The sample was fixed onto a manual rotation stage and measured every $10^\circ$ for both tilt angle configurations (polar and azimuthal). The size of the illumination spot was about $3 \times 5$ mm, the measured samples were about $2 \times 2$ cm. The measured transmission values were transferred into RGB values with a homemade Matlab script.

Computations. Far-field computations were done with RCWA from 400 to 700 nm, in 0.5 nm steps. Zero order transmission computations were done for varying incidence angles (from $-60^\circ$ to $10^\circ$) and varying period (from 100 to 250 nm, 0.5 nm step) and length (10 nm to 220 nm, 0.5 nm step). The near-field simulations were done with SIE. First a far-field zero order transmission spectrum was computed (400 nm to 700 nm, 0.5 nm step), then a near-field map of the structure at the indicated points (see Figure 4) was done (precision of 0.5 nm). The intensity is plotted logarithmically.

Conflict of Interest: The authors declare no competing financial interest.

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