STRUCTURAL COLOR OF METALLIC SURFACES

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Abstract
Nano structuring of metallic surfaces shows surface colors unusual for a given material. This study presents
an overview of possible approaches to achieve desirable color changes. The nano structured relief
structures prepared by means of electron beam lithography process are presented. Optical design and
simulation of optical properties, data preparation for e-beam patterning, parameters of the writing process,
and technological issues are presented in detail. Finally, real examples of structures that exhibit surface
color changes are presented and discussed.

Keywords: nano structures, structural color, metallic surface; e-beam lithography.

1. INTRODUCTION

Smooth metallic surfaces are generally very shiny and reflect colors that are characteristic to the material.
Regular structuring of the surface may exhibit different colors that are mainly dependent on the structure and
its parameters rather than the material itself. This contribution seeks to present a study how the colored
metal surface can be achieved.

We have reported abilities of the e-beam patterning a few times within the scope of the Metal Conference
Series [1], [2], [3]. The actual contribution is focused on structural colors of metallic surfaces.

The structural color of colorless matter is a well known phenomena; a detailed analysis was presented e.g.
by van Renesse [4]. Within this contribution we leave apart the traditional rainbow diffractive colors and
interference colors of thin layers. We will focus on reflective (metallic) structures that have relatively deep
relief (essentially deeper then reflective gratings tuned to the first diffractive order) [5] and simultaneously
they exhibit intensive zero order diffraction phenomena. Such gratings (zero order gratings) have low period
(generally below 450 nm) and they were reported mainly as transparent structures [6].

2. OPTICS

First, let us assume a regular relief grating with a rectangular reflective profile. Period of the grating
being \( \Lambda = 1000 \) nm and its depth is about \( h = 125 \) nm. The spot light (assuming visible light with the
wavelength range \( \lambda \in (400; 700) \) nm coming to the surface is bent (diffracted) to directions given by the
grating equation. When the grating depth is tuned to the first diffraction order (as in the above example), only
a minor part of the coming light is reflected to the zero diffraction order. It is possible, by increasing the
grating depth, to enhance the zero order mode. As the zero order mode is spectrally dependent, different
color response in specular reflection can be achieved by tuning the profile depth.

2.1. All But Zero Order Mode (ABZO Mode)

Now, let us turn to a similar structure (similar sizes) but instead of a regular grating, let us take a quasi
random structure. Such a type of structure can be a computer generated hologram (CGH) that bends the
incoming light to the desired directions. In this configuration the light diffracted to directions defined by the CGH structure will contain all the spectral colors with one selected color attenuated (that one which has the enhanced zero order response). This configuration may be regarded as an all-but-zero-order mode (ABZO mode). This situation is shown in Figure 1, where the light spectral intensity is plotted versus the depth of the relief. Colors of the six selected cases (wavelength 420 - 700 nm) do not represent directly the spectral color; still they are somehow close to the spectral colors.

![Fig. 1 Intensity of light reflected from the structured surface: specular reflection (above) and scattered reflection (below); colors are only exemplary.](image)

By exploring four cases of relief depth (200, 260, 330 and 400 nm) we can expect the following color tint of the scattered reflection:
- at 200 nm: blue violet is missing, expected response is yellowish or orange-red;
- at 260 nm: green and yellow is missing; expected response is purplish (magenta) or blue violet;
- at 330 nm: red is missing; expected response is bluish or cyan;
- at 400 nm: red and blue violet components are missing, expected response is green or yellow-green.
The spectral response for those four cases is shown in Figure 2 (similarly to the previous figure, the plot colors represent the color response only approximately).

In fact, the sequence of ABZO mode colors is similar to the sequence of interference thin-layer colors; with refractive index of air (approximately 1.00). Furthermore, the ABZO mode colors should be rather colorful as now, the surface reflectivity is much higher. Intuitive and rule-of-thumb interference color sequences were compared earlier [7] (it can be accessed also through [8]).

Fig. 2 Spectral intensity of light reflected from the structured surface: scattered reflection (relief depth 200 - 400 nm); colors are only exemplary.

2.2. Multi Step Zero Order Mode

The approach described in the previous section may be extended to even deeper reliefs (up to some 1000 nm). Now, we can get one more degree of freedom. We can imagine multiple steps structure with the step level height tuned to the $\lambda/2$ for a selected wavelength. Assuming the wavelength $\lambda = 600$ nm and preparing the four level structure with the depths of 0, 300, 600 and 900 nm, we expect to obtain a sharper frequency response.

3. E-BEAM PATTERNING

We had been studied the structural colors since a couple of years. However, with the improvement of patterning technology in the last years, the results may become much more pronounced. E-beam lithography is, in a traditional way, a binary process. Resulting structure may have flat areas with very sharp transition. This kind of technology is very suitable for the proposed relief structures. However, one can see two limitations. First, if several colors are expected within one sample (relief of different depths are expected), then the binary approach is not appropriate. Second, the multi step zero order mode is not achievable at all.

As an alternative, one can explore a relief e-beam technology, where the depth of each element can be adjusted independently. Here, we face the problems of writing speed, the homogeneity of the stamp (basic shaped beam spot in the case of shaped-beam system) and the electron scattering (proximity effect).

We used both shaped beam and Gaussian beam tools for the patterning. The key factor in the case of the shaped beam writer (Tesla BS600) was a successful development of the enhanced TZ writing mode (e.g.
(9) and the progress in stamp homogeneity adjustment (10). Later on, a new Gaussian beam patterning tool (Vistec EBPG5000plusES) was installed. We have got comparable results using this new tool for the origination.

Basic lithographic approaches to prepare required structures are schematically depicted in Figure 3. First, the basic binary structure is shown (a), where the relief depth $h_{bin}$ is approximately equal to the thickness of the original layer $h_0$. Next, when the relief e-beam lithography is in use, two cases may be adopted. Let us assume the positive tone resist. Then, either the resist is locally fully developed (bottom reference) with variable upper part of the relief (b). Or, the resist is locally non-exposed (top reference) and the lower part of the relief is variable (c). In the later cases, one should keep in mind that only the upper part of the resist is available to the patterning as the sensitivity curve in the lower part of the resist layer is very sharp. Taking into account these limitations, one may consider the combination of both approaches (b) and (c) such that large gamut of colors may be obtained within one sample.

![Diagram of various approaches to pattern the thin film resist layer: binary structure (a), relief structure with bottom reference (b), and relief structure with top reference (c).](image)

The relief structure prepared in the thin resist layer may be covered by metal deposition (e.g. sputtering or vapor deposition) and then it can be further processed by standard electroforming processes.

4. RESULTS

The final relief structures (by atomic force microscopy (AFM) scans) are shown in Figure 4 (binary structure) and in Figure 6 (relief structure top referenced) together with the appropriate depth histogram (Figure 5 and Figure 7). It may be observed that the binary structure relief is suitable for the given purpose (the histogram is in some degree distorted by AFM artifacts). On the other hand, the relief structure does not show the flat bottom part and the coloring effect is very weak.
Fig. 4 AFM image of a binary structure. Designed pixel size is 500 × 500 nm². Shown is a detail of some 10 by 10 um².

Fig. 5 Depth histogram of the structure from the Figure 4 shows pretty good binary levels and a depth of approx. 561 nm.

Fig. 6 AFM image of a relief structure. Designed pixel size is 500 × 500 nm². Shown is a detail of some 5 by 5 um².

Fig. 7 Depth histogram of the structure from the Figure 6 shows the smooth top level and a variable bottom level (the depth of approx. 480 nm).

The next image (Figure 8) is a multi step structure imaged by scanning electron microscopy (SEM). Even if measurements of the relief were not performed, one can recognize that technological issues prohibit the quality of results. In fact, the coloring response of this structure was practically negligible.

An example of a complex DOVID structure (Diffractive Optically Variable Image Device) is shown in Figure 9. The sample is covered by a thin Silver layer and it shows both diffractive rainbow colors inside the image and the structural all-but-zero-order color (yellow or gold) on its border.

5. CONCLUSIONS

A new approach to prepare a structural color of metallic layers was shown to be feasible. The best results were achieved with a binary relief type while both the multi color approach and the multi step approach would need more investigation, mainly as the quality of the patterning technology process is concerned.
Fig. 8 SEM image of a multilevel structure. Designed pixel size is $500 \times 500$ nm$^2$. Total depth is approx. 1050 nm. Shown is a detail of 8 by 5 um$^2$.

Fig. 9 Sample structure covered by Silver showing both diffractive rainbow colors inside the image and the structural color (yellow or gold) on its border. Image size is approximately $20 \times 12.5$ mm$^2$.

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LITERATURE


