Scalable physical coloration

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\begin{abstract}
Methods to produce colored surfaces using physical mechanisms are proposed, with aluminum used as a demonstration vehicle. Our approach aims to achieve tunable, vibrant colors through the interaction of three well-established physical mechanisms of color formation, namely (1) resonant scattering and interference effects in a nano-structured surface (e.g., via anodization of aluminum), (2) plasmonic resonances in metal nanoparticles, and (3) spectrally selective absorption enhancement in ultrathin films, such as amorphous germanium and carbon. We provide proof-of-concept by fabricating and characterizing representative aluminum-based samples showing vivid colors throughout the visible spectral range.
\end{abstract}

1. Introduction

Color is the most ubiquitous facet of human visual perception, yet the methods currently used to color surfaces are still rather limited when compared to the myriad possible coloration mechanisms. Chemical coloration, using paints with pigments and/or dyes, is the most widespread method for producing colored surfaces at home or in industrial applications. Paints consist of suspensions of absorbing molecules or particulates in an otherwise neutral binder medium [1–3]. The spectral absorption of each of the chemicals and their relative concentrations determine the final color of the paint. Additional materials can also be added, including particulates [4–6] (metals or dielectrics such as titania and alumina) aimed at enhancing the scattering of light within the composite matrix. Solvents and stabilizers may also be added to control the viscosity and to enhance durability [1–3, 7]. These chemicals produce colors via the selective absorption of light by molecular electronic resonances. Certain portions of the incident light spectrum are absorbed and the remaining light that reaches the eyes upon reflection or transmission determines the object's perceived color. Chemical coloration certainly has its benefits, but it is often desirable to use physical rather than chemical mechanisms for manipulating the light spectra to generate beautiful, saturated colors, which is shown to be possible and discussed here. Physical coloration is a quickly growing field, with many new and different strategies being used [8–14]. Although these physical mechanisms are generally applicable to most solid-state materials, for greater clarity we will use coloration of an aluminum surface as a specific demonstration vehicle.

Aluminum is a commodity of paramount and growing importance to modern industry. It is often desirable to color aluminum surfaces for both aesthetic reasons and to protect the aluminum part [15]. Currently, industrial coloration of aluminum surfaces utilizes one of two basic processes, both of which are based on paints or dyes. The first process is widely used in the automotive and aircraft industries and consists of coating the aluminum with an epoxy primer that is then coated with paint. The primer’s function is to protect the surface from the chemicals in the paint and to provide a smooth surface onto which the paint can adhere. The second method involves anodizing the aluminum surface to form a porous alumina film coating. A dye is then inserted into the alumina film pores, followed by submersion into a thermal bath that causes sealing of the pores, trapping the dye inside [15].

A few shortcomings exist in this approach. First, pigments and dyes often consist of molecules that are poisonous and whose production involves environmentally unfriendly methods with large carbon footprints. They are susceptible to degradation due to exposure to chemicals in detergents and cleaners, to heat, humidity, and the elements, and to UV radiation from the sun [16–22]. In addition, the current chemical approach for coloring surfaces relies exclusively on selective absorption and thus requires optically thick coatings in order to produce pure and
vibrant colors. Such optically-thick films are not only more prone to cracking and peeling damage, but also add considerably to the final weight, affect thermal properties, and change the overall mechanical properties of the part [1–3].

To address these shortcomings, physical rather than chemical techniques can be deployed for manipulating the light spectra that is reflected off aluminum surfaces to generate desirable colors. In this paper, we investigate the use of three physical mechanisms to achieve this, as illustrated in Fig. 1. They are, namely, (1) order-dependent diffraction and interference, (2) localized electronic processes in metal nanoparticles with plasmonic resonances, and (3) ultra-thin absorbers with extraordinary spectrally-selective attenuation and enhancement. We implement combinations of these mechanisms in structures consisting of nanoparticles embedded in Anodized Aluminum Oxide (AAO), as well as thin film absorbers deposited either directly onto Al, or onto AAO on Al.

Fig. 2 shows real samples of these structures achieving a wide spectrum of impressive surface colors. In Fig. 2(a) and (b) ultrathin carbon and germanium coatings, respectively, lead to both sharp and subdued angle-independent colors when applied directly onto different surface finishes of aluminum. In these samples, the ultrathin absorbing layer gives rise to complex phase shifts at the absorber-metal interface causing interference in vastly subwave-length absorber thicknesses[23], as will be discussed in Section 2.1. Fig. 2(c) shows iridescent finishes produced via the use of a carbon film on AAO on Al. It has been suggested that this film could cause a Fabry-Pérot cavity effect between it and the Al substrate [24], in addition to the same complex phase shifts from Fig. 2(a) and (b), from carbon that gets inside the AAO pores and contacts the Al. In Fig. 2(d) plasmonic gold nanoparticles are introduced into the AAO pores to generate magenta coloration. The AAO provides both a vehicle for the nanoparticles, as well as a scattering matrix to increase the effective extinction caused by the nanoparticles. Other colors can also be realized with nanoparticles of different metals and sizes [25,26].

2. Results: physical mechanisms for surface coloration

2.1. Spectral selective absorption and color enhancement in ultrathin films

Beautiful coloration of AAO, bare aluminum surfaces, and other metals such as gold have been demonstrated via deposition of ultrathin films of highly absorbing materials. In experiments done by Yue et al. [24], a 15 nm Al layer was deposited on top of AAO to produce a vibrant color filter. The authors attribute that result to the formation of a high-finesse Fabry-Pérot cavity in the AAO. In experiments done by Katz et al. [23], 7–20 nm layers of Ge were deposited on Au to produce saturated, non-iridescent colors. The authors attribute these colors to a complex phase shift at the Ge-Au interface, allowing the Ge film to be far below wavelength. Experiments by Wang et al. [27] have shed more light on the importance of the interaction between the absorbing film and substrate. They showed that saturated colors could be obtained and tuned by lining the inside of the AAO pores with a layer of glassy carbon and that only the bottom portion of the vertically standing glassy-carbon nanotubes (closest to the metal substrate-AAO interface) was relevant in determining the color.

Both amorphous C (α-C) and amorphous Ge (α-Ge) are lossy materials in the visible range by themselves, owing to electronic band gap excitation. α-C has a band gap largely influenced by the relative percentage of sp² and sp³ bonds in the deposited film, which is highly dependent on the film deposition method; evaporation puts the band gap of α-C at 0.4–0.7 eV while for various other methods it can be as high as 2.4 eV [28]. Similarly, α-Ge has a band gap in the infrared, with a direct transition at 0.6 eV (in contrast to the same transition at 0.8 eV in crystalline Ge [29]), although it has been shown that evaporation conditions can make it as low as 0.4 eV [30,31].

Visual inspection with the naked eye of our carbon-coated aluminum (Fig. 3(a)) and germanium-coated aluminum (Fig. 3(b)) samples reveals that iridescence can be drastically reduced in such structures. The origin of this is as follows: in regular thin film interference, the thin film has a thickness of the order of the wavelength, so when the film is viewed at some angle away from the normal, the path length is now very different than the path length at normal incidence compared to the incident wavelength. However, when the thickness of the film is up to an order of magnitude smaller than the wavelength, even a relatively large viewing angle only increases the path length a small amount compared to the wavelength, and thus has roughly the same optical response. This is a very useful benefit of the complex phase shift occurring at the absorber-metal interface for ultra-thin films.

It is also worth noting the physical significance of the connection between the specific shapes of the reflectance curves and the color and brightness of the samples in Fig. 3. First, as the film thickness is varied, it is clear that the wavelengths of reflectance minima and maxima change as a result of interference; this straightforwardly determines the color in the above samples because a reflectance peak indicates the remaining light that reaches an observer (for example, the 100 nm blue sample in Fig. 3(a) has a peak in the blue region of the visible spectrum and thus appears more blue, while the 10 nm red sample in Fig. 3(b) has a peak in the red region and appears more red). Due to the same logic, if a sample has a reflectance spectrum that is relatively flat across all wavelengths, it will appear “washed out” and grey, since all colors are reflected equally and no color will dominate (as in the 25 nm grey sample in Fig. 3(b)). Second, another effect of increasing film thickness is that, while the color changes, the overall brightness also dims. This is inherent to the nature of interference in this type of sample; while typical thin-film interference relies upon phase differences as incident light travels through the medium, the current structure is able to achieve reflection at much thinner films due to the complex phase shift caused by it being a lossy material. However, this comes at a cost: as the light travels through the lossy material it loses intensity, meaning that the magnitude of the reflected light is smaller and the samples appear not as bright (as is apparent by comparing the 5 nm yellow sample in Fig. 3(b), which has a peak reflectance of
Fig. 2. Samples fabricated using the proposed approaches for physical coloration of aluminum and alumina surfaces. The different rows shown here illustrate various combinations of thin-films (amorphous carbon and germanium) or absorbing metal particles (such as gold) with nanocorrugated (AAO) or flat (aluminum/silicon) substrates used in this paper. The left column displays various colors achieved at near-normal incidence for each method. The middle column displays a schematic for each type of structure. The right column displays oblique incidence, as the color of some structures are viewing-angle dependent, as shown in (c).

~80%, to the 20 nm cyan sample in Fig. 3(b), with a peak reflectance of ~40%.

Fig. 4 reports simulated specular reflectance spectra at normal incidence for amorphous C (top panel) and amorphous Ge (bottom panel) deposited on Al as a function of film thickness. The simulations were done using a standard Transfer Matrix Method approach [32,33] in Mathematica with optical values taken from Jellison [34] and Hagemann [35]. A dramatic change in color and higher saturation can be seen for the C samples, as observed experimentally in Fig. 3(a). It is worth noting that a small change in film thickness – i.e. from 0 to 55 nm in steps of 5 nm – results in a dramatic change in the spectrum and perceived color. The color-labeled curves in Fig. 4 show a good agreement with the experimental data reported in Fig. 3 for both C and Ge.

2.2. Structural coloration via resonance, scattering, and interference

AAO can also be used to produce structures for coloration. By itself (or on its Al growth substrate), AAO has slight color, but the color is pale due to its low absorbance in the visible range; however, due to its unique and tunable topology, AAO offers many paths to color production. Fig. 5(a) illustrates some of the relevant physical phenomena at play in this structure, including various diffraction, Rayleigh scattering, and optical resonance effects.

Diffraction stems from the periodicity of the AAO, similar to what is observed in 2D photonic crystals. Because the AAO pores are oriented normal to the aluminum surface, diffraction occurs primarily in the surface (longitudinal) plane, which favors the formation of diffraction colors at steep angles of observation [36,37]. Similarly, Zhang et al. demonstrated that clever use of alternating anodization parameters can create a 1D photonic crystal that gives rise to strong band filter peaks [38,39] that can be used for bright coloration in pure AAO.

Scattering arises due to surface roughness and the inherent porosity of the structure. In fact, Zhang et al. found that due to Rayleigh scattering in AAO, there was a symmetry-breaking such that incident light going through the same material from opposite directions had different reflection spectra [40]. Because Rayleigh scattering due to AAO is dependent upon the pore parameters, this presents another variable that can be tuned to selectively scatter part of the visible wavelength.

Optical resonances include both Fabry-Pérot effects (i.e. due to multiple passes of light reflected at the air-AAO and AAO-aluminum interfaces) and waveguide modes, which arise from confinement of light into the regions of alumina between pores, similar to an optical fiber (Fig. 5(a)). Fabry-Pérot effects are discussed in more detail below.

The AAO lattice parameters, namely, the mean pore diameter (D), pore–pore separation (p), and film thickness (t) (Fig. 5(b)), are controllable by varying the anodization cell voltage, temperature, as well as electrolyte type and concentration [41–43]. First, pore diameters can be enlarged via wet etching [44]. This process maintains the lattice period while decreasing the effective refractive index of the layers. Second, pore separations ranging from ~20 nm up to more than 400 nm have been demonstrated [43]. It is also possible to employ conformal coating techniques, such as chemical vapor deposition (CVD) or atomic layer deposition (ALD) [45,46], to coat the inside of the pores with dielectric materials to alter the effective refractive indices. These structural parameters can be used to control the spectral properties of the AAO lattice, enabling optical responses to be tailored to different bands of the visible spectrum [36,37].

For AAO produced via established anodization processes (pore diameters small compared to incident wavelengths), the most prominent coloration mechanism observed is thin-film interference. This thin-film effect occurs in the out-of-plane direction due to multiple reflections inside the AAO film, bounded on one side by the Al substrate and by air on the other side, leading to the formation of viewing-angle dependent colors (iridescence). However, the effect is weak because alumina has a relatively
low index of refraction, exacerbated by AAO’s porosity. This manifests itself in poor color contrast, particularly in the case of a polished Al substrate where most of the incident light is reflected.

However, recent works [23,24,27] have suggested that a thin, highly absorbing layer on top of the AAO could dramatically enhance the color contrast with subdued iridescence. We have tested this principle with a thin AAO layer created by anodization of the bare Al substrate before depositing the absorber layer. However, we found that iridescence occurs when the AAO layer is relatively thick (> 50 nm). This is evident by comparing the two samples in Fig. 6. Saturated colors were obtained in these absorber/AAO/Al samples as shown in Fig. 6, which consist of a carbon layer placed atop an AAO layer. The sample in Fig. 6(a) has a thick (~600 nm) AAO layer and thus produces iridescence, while the sample in Fig. 6(b) has a thinner (~200 nm) AAO layer which is not as iridescent, as evidenced by examination of the total and specular reflectance curves for each sample. In fact, the AAO layer can be made significantly thinner and changed continuously, providing more granular control of color, while still producing saturated colors.

These encouraging results demonstrate a larger physical parameter space, including single vs. multilayer coatings, varying film thickness, and material choice for both substrate and dielectric films. However, these ultrathin films and thinner AAO layers are susceptible to scratches and dents and may not offer sufficient protection to the aluminum surface in more demanding applications. To counter this problem a protective layer could be added such as spin-on glass/sol gel ceramics atop the ultrathin film. Other methods for ultrathin coatings inside the AAO pores can be accomplished, for instance, via electro-less metal and semiconductor deposition [47–51] as well as pyrolysis of carbon sources (e.g., CH₄) [27,52,53]. While it is known that glassy carbon on alumina [27] can achieve good material hardness, the process can be altered from pyrolysis carbon coating to sputter or solution-deposited coating, which does not alter the structural properties of the aluminum alloy while improving adhesion.

2.3. Physical coloration via quantum plasmonic resonances

Surface plasmons are surface charge density oscillations occurring in the quasi-free electron gas present within a metal film or nanoparticle [54]. These surface oscillations are resonant phenomena depending on the properties of the metal, the surrounding dielectric, and the nanoparticle size.

Nanoparticles can be easily integrated into an AAO matrix (Fig. 7(a)). The interplay between the AAO matrix (dielectric) and the surface plasmon resonances (SPRs) in nanoparticles can generate well-defined colors [Fig. 7(c)] [25,26]. SPR-colors are generally not iridescent because they do not arise from conventional (i.e., low-loss) interference effects, but rather from strong, size-dependent optical responses (i.e., scattering, absorption, confined plasmons) of electron excitations in the nanoparticles (Fig. 7(b)) [55].

The color of the hybrid AAO/SPR structure can be tuned by varying the mean diameter of the metal nanoparticles, as well as the pore size, pitch, and thickness of the AAO dielectric medium. In a proof-of-concept experiment, “yellow” and “pink” colored samples (Fig. 7(c))
were fabricated via deposition of silver nanoparticles in AAO [25]. The nanoparticles were deposited into the pores simply by dip-coating AAO-on-aluminum into a liquid dispersion of nanoparticles. Heating the sample above 400 °C caused the particles to agglomerate into larger ones, thus changing the color of the coating layer from yellow to pink. An even broader range of colors was obtained by Chen et al. via electrodeposition of Ni nanoparticles in AAO [26]. Metallic and dielectric nanoparticles can be inserted into the AAO pores via other methods, including electro-less deposition [47,48,56], evaporative and sputter coating [57], and dip-coating [25]. Fig. 7(e) shows SEM images of the sample in Fig. 2(d) which was fabricated by dip-coating with 10 nm Au nanoparticles. Visual inspection of the sample shown in Fig. 2(d) (and inset in Fig. 7(f)) reveals low iridescence and a saturated magenta color. This is confirmed by the reflectance measurements in Fig. 7(f), in which the total and specular reflectance curves are nearly the same, implying low iridescence. Additionally, the saturation in color is confirmed by the sharp increase in reflectance occurring around 600 nm. The subdued reflectance peak centered around 400 nm (providing a small amount of blue) is responsible for the magenta tone; without it the sample would appear red. It is also noted that the difference in reflectance spectra between AAO with and without nanoparticles occurs in the range of the plasmon resonance of the nanoparticles [25].
3. Conclusion

In conclusion, we have presented a general physical method that lies at the intersection of three well-known physical mechanisms to generate vivid colors inspired by nature. We have discussed ways each mechanism can be tuned separately, as well as their respective strengths and weaknesses. The importance of our work is encompassed by two aspects: its tunability and potential for scalability.

The success in coloration with ultrathin absorbing films on Al or AAO/Al, establishes a proof-of-concept technique for achieving a range of interesting colors. The process allows for color tuning via control of the deposited absorber thickness and material as well as the thickness of the (optional) AAO layer formed prior to absorber coating. In addition, we have investigated the production of an absorbing medium by incorporating plasmonic metal nanoparticles into an AAO matrix. It is shown that saturated colors with low iridescence can be obtained, even in relatively thick AAO films. We discussed the parameters that can be used to tune this coloration mechanism, such as nanoparticle material, size, number density, and shape. Combinations of the mechanisms investigated here could also be used; for example, metal nanoparticles deposited into the AAO layer in Absorber/AAO/Al samples before evaporation of the absorber could provide another control parameter for coloration and taming iridescence.

Importantly, all the fabrication techniques used in this paper are scalable processes that could be or are already used by industry. AAO is already produced on large scales. The absorber coatings were obtained by room temperature evaporation, and thus did not require heating of the aluminum substrate. The need for heating is undesirable in industrial processes because it can alter the structural properties of the aluminum part. To account for the fragility of the ultrathin absorbing films explored here, several strategies could make them more robust, such as covering the surface in a non-color-altering protective layer such as a spin-on glass or epoxy. This would also protect against any natural delamination. It is currently common industrial practice to embed AAO pores with dyes; similarly, the same technique could be used for the AAO/nanoparticle structures we have reported on. There is good agreement between the measured colors of our evaporated carbon coatings and thin-film simulations based on the transfer matrix method using an approximate value for the carbon dielectric constant spectrum. This suggests that coating parameters can be determined to accurately produce the color-by-design.

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References

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