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Color Engineering of Silicon Nitride Surface to Characterize the Polydopamine Refractive Index

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Abstract: A simple methodology to generate polydopamine (PDA) surfaces featured with color due to the thin film interference phenomena is presented. It is based on depositing ultra-thin films of polydopamine on a Si/Si_3N_4 wafer which exhibits an interferential reflectance maximum right at the visible/UV boundary (~ 400 nm). Therefore, a small deposit of PDA modifies the optical path, in such manner that the wavelength of the maximum of reflectance red shifts. Because the human eye is very sensitive to any change of the light spectral distribution at the visible region, very small film thickness changes (~30 nm) are enough to notably modify the perceived color. Consequently, a controlled deposit of PDA, tune the color along the whole visible spectrum. Additionally, good quality of PDA deposits allowed us to determine the refractive index of polydopamine by ellipsometry spectroscopy. This data can be crucial in confocal skin microscopic techniques, presently used in diagnosis of skin tumors.

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Introduction

Physical interaction of light with structured surfaces is the origin of many bright colors found in nature.[1] Regarding the mechanism, thin-film interference is perhaps the simplest source of structural color.[2,3] The iridescent color in soap bubbles is the simplest example found in the nature. However, in case that absorption and interference combine, the color palette notably increases. Such is the case of the bright colors of peacock tail feathers caused by the 2D organization of melanosome granules or the brilliant blue of the wings of *Morpho* butterflies species originated by the arrays of ridges and lamellae of chitin in the wing scales.

Presently, it is possible to mimic the colors of nature thanks to the thin-films growth techniques.[4, 5] Actually, the control of layer thicknesses affects the surface color and then to the aesthetic of the surface, which has repercussion in the development of devices for which the appearance is relevant.[6] In addition, the development of surfaces with a high control of the color through a precise and uniform film thickness can be considered a smart approach for the characterization of the optical properties (complex refractive index or dielectric function)[7] of emerging materials in science.

Polydopamine is a synthetic melanin with similar physical properties to its natural counterparts.[8] Among them, the broad UV-Vis absorption, is determining in the skin protection against the sun UV radiation.[9, 10] Polydopamine has been essential in the progress of many diverse material areas due in part to its strong affinity for a great variety of surfaces together with its versatile chemistry which permits multiple functionalization approaches.[11, 12] It has been stated that polydopamine has a higher refractive index value than many synthetic polymers. [13-17] Unfortunately, there is still controversy about the refractive index value.[14, 16, 17] The reported values were mainly obtained for polydopamine colloidal dispersions.[17, 18] Nowadays, accurate determination of the polydopamine refractive index is necessary since polydopamine has a central role in the development of materials for optical applications.[19,16] Besides, the examination of skin and the diagnosis of melanomas can be based on the use of non-invasive optical biomedical imaging techniques such as reflectance confocal microscopy, which examines tissue back-scattering from structures with endogenous contrast such as melanin to seek for abnormal refractive index boundaries associated to melanomas.[20] Consequently, advance in melanoma diagnosis is linked to the melanin refractive index value estimation.

In the context of color production by interferential phenomenon, films of polydopamine nanoparticles have been prepared by either evaporation or spray coating of aqueous dispersions polydopamine nanoparticles, achieving colored surfaces that perfectly mimic the striking colors of avian feathers.[9, 18, 21] On the other hand, the oxidative dopamine polymerization in a basic aqueous medium has been established as a simple methodology to coat surfaces regardless of their material nature. The surface polydopamine modification is a bio-inspired process by the mussel adhesion chemistry.[11] However, the in situ polydopamine coating during the polymerization process represents a seldom explored strategy in the generation of surfaces characterized with color.[15] In this work, silicon wafers were coated with a polydopamine film by using Cu_2SO_4/H_2O_2 as trigger of the dopamine polymerization and different colors such as yellow, purple, blue, and greenish blue were obtained by varying the polydopamine thickness.

Herein, we accomplish a methodology to generate colored surfaces by depositing an ultra-thin film of polydopamine on a silicon nitride substrate featured with reflectance in the bluer visible boundary at 400 nm. We advance that simply by coating with a uniform polydopamine film of a precise thickness (from 30 to 250 nm) we could uniformly tailor the reflectance of the surface along the visible wavelength range. These uniformed surfaces in color and concomitant in thickness were characterized by scanning electron and atomic force microscopies and used to determine the refractive index of polydopamine by ellipsometry spectroscopy.

Results and Discussion

The use of a substrate which exhibits reflectance in the visible region of the electromagnetic spectrum represents a seldom explored choice in the design of surfaces featured with color.[22] The reflectance position in the visible spectrum of a thin film of silicon nitride on a silicon substrate is function of its thickness.[23] We hypothesize that the deposition of a controlled thin film of polydopamine in this kind of substrate would increase the optical path, which in turn would lead to the notably modification the reflectance properties vs. wavelength of the multilayer structure. Additionaly, these colored surfaces would allow the determination of the refractive index of polydopamine by spectroscopic ellipsometry. The herewith describe experimental approach would be an outstanding methodology for the generation of surfaces featured with color by thin film interference phenomenon.

Silicon nitride coating with a thin film of polydopamine

The silicon nitride substrate used in this work, named hereafter silicon-silicon nitride wafer (SSNW), consists in a wafer of crystalline silicon (520 µm) coated in both sides with a thin layer (200 nm) of silicon nitride which was deposited by chemical vapor deposition. We have focused on the polished side to study the polydopamine modification. Its surface has a violet color as result of a second order interferential reflectance band located at 400 nm. As we said above, the position of this reflectance band is function of silicon nitride thickness.[23] As the reflectance band is placed right at the blue to UV edge, any small deposit will red-shift the color of the samples, in such manner, that just by ocular inspections, it would be possible to determine the thickness modification due to the deposit of successive polydopamine films.

Polydopamine is obtained by dopamine oxidative self-polymerization in a basic or oxidative medium. The polydopamine film growth can be controlled with polydopamine concentration and polymerization time. So, coating of silicon with a polydopamine film of approximately 20 nm in thick has been reported after 10 hours of polymerization.[24] In order to grow thin polydopamine films with control in the thickness uniformity over the silicon nitride substrate, similar conditions were used. Sections of SSNW of ca. 1 cm^2 were fixed at the bottom of an open-air flask and put in contact with a solution of dopamine hydrochloride (2mg/mL) in aqueous trizma buffer solution (pH 8.5) for 10 h with continuous and controlled mechanical stirring. Scheme 1 shows the protocol for the polydopamine coating process. Each substrate underwent different polymerization cycles (up to 4 cycles).

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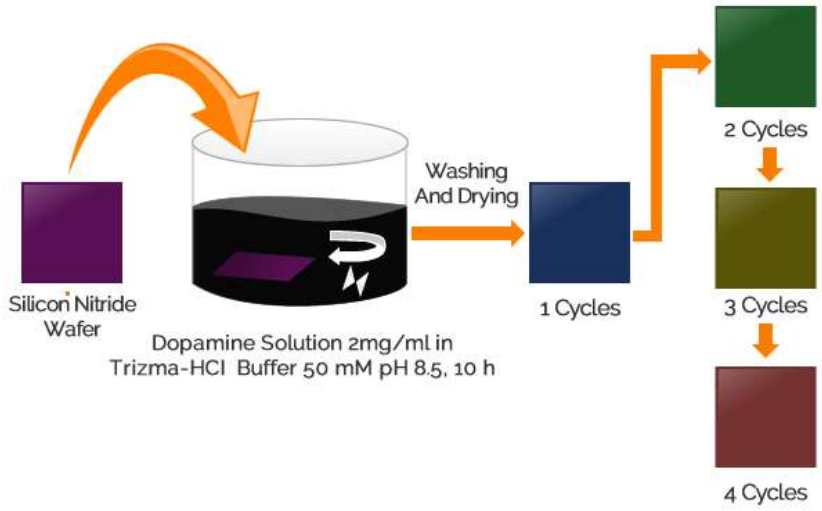

Scheme 1. Illustration of the protocol to tune the optical properties of silicon nitride surface with a polydopamine coating of different thickness.

Importantly, polydopamine modification led to an abrupt change in the surface color as it was initially supposed. The color surface shifted from violet to blue when the wafer underwent a first polymerization cycle. Moreover, the surface color could be tailored along the visible range by controlling the number of polymerization cycles. The experimental conditions, polymerization time and dopamine concentration, were the same for all polymerization cycles. The wafers were observed at daylight and display uniform colors along a significant surface (at least 1 cm^2). The colors of the wafers after being exposed up to four polymerization cycles are shown in Figure 1, blue for one, green for two, yellow for three and reddish when the wafer underwent four polymerization cycles.

Figure 1. Image showing the surface colors of SSNW in daylight. Each surface color is obtained after exposing the SSNW (left surface) to different polymerization cycles (up to four). From left to right: violet (SSNW), blue (one cycle), green (two cycles), yellow (three cycles) and reddish (four cycles).

Surface characterization

The successfully polydopamine coating of the SSNW was corroborated through Raman spectroscopy. The Raman spectra (data not shown) of the surface after the different number of polymerization cycles presented only the two characteristic broad bands at 1380 and 1600 cm^{-1} of polydopamine.[25]

The surfaces were afterwards characterized by scanning electron (SEM) and atomic force microscopy (AFM). Firstly, the SEM image of the surface of bare SSNW does not present any kind of structuration. It is a smooth surface as it is shown in Figure 2A. It can be also seen that the silicon nitride film has an average thickness of ca. 200 nm. Upon a first polydopamine polymerization cycle, there is a dispersion of irregular aggregates of polydopamine nanoparticles distributed along the surface as it is shown in Figure 2B. The image of surface in Figure 2C was selected because there is an area of SSNW without coating together with part of the surface modified with polydopamine. It can be seen, when the interface between both zones is compared, that the coating is formed by a continuous film of polydopamine that acts as support of these aggregates. These aggregates are formed in solution during the polymerization to later be deposited on the surface, while the dopamine polymerization continues.[22]

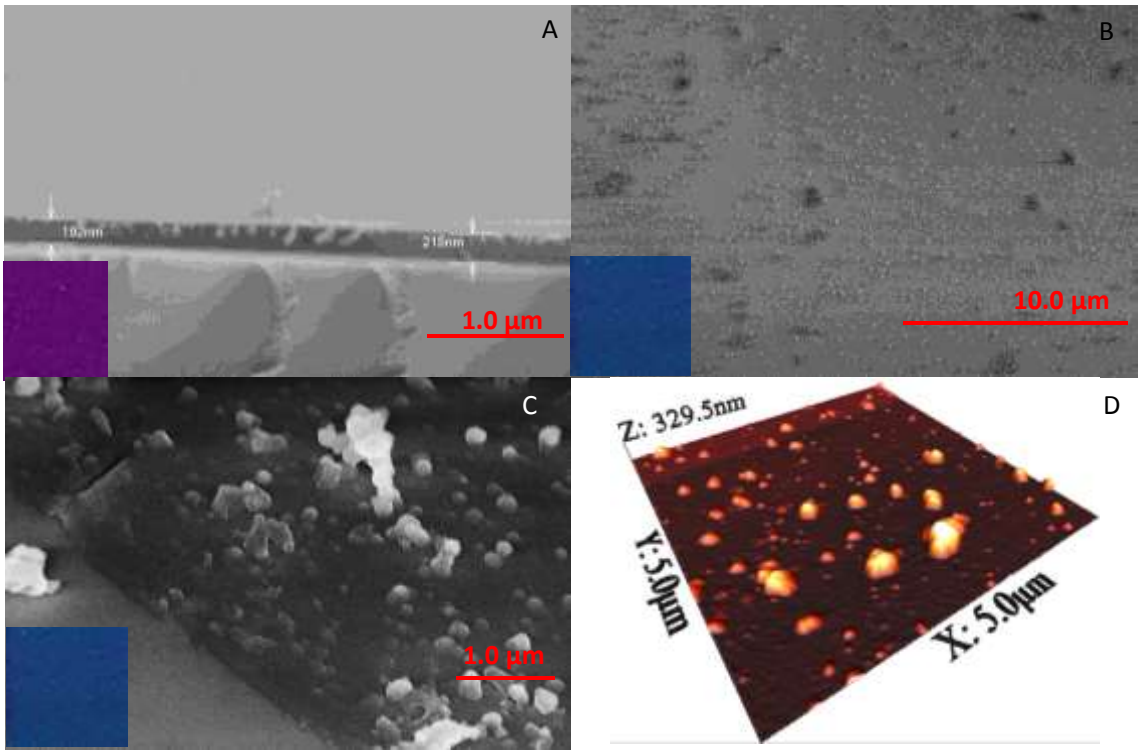

Figure 2. A) SEM image of the top surface and the perpendicular section of the SSNW. B and C) SEM images of the top surface of the silicon nitride wafer after the first polymerization cycle. In image C, an area without polydopamine (bare silicon nitride surface) along with the continue film of PD that coats the SSNW can been seen. D) AFM image of the surface after undergoing a first polymerization cycle.

The subsequent polymerization cycles led to the increase of number, size and inhomogeneity of the polydopamine aggregates dispersed on the surface as can be seen in the SEM images of the surfaces, Figure S1 (Supporting Information). The presence of these aggregates has a detrimental effect in the specular reflectance, since they

scatter light which makes that the observed surface texture be more diffusive (or "less metallic") and therefore less specular with the increase of their number and size.

Subsequent, analysis of surface topography after the first polymerization cycle by AFM, Figure 2D, shows that aggregates of polydopamine nanoparticles are randomly distributed over a rough cement of polydopamine.

The polydopamine thickness was determined by profilometry and AFM respectively for the blue (1 polymerization cycle) and green (2 polymerization cycles) surfaces by a shape scratch on the surfaces. The profiles of polydopamine height area are shown in Figure S2 (Supporting Information). The average polydopamine thickness film was 30 ± 23 nm and 85 ± 39 nm respectively for the blue and green surfaces.

Optical Properties

As it has been said, the obtained color of the PDA coated samples is a consequence of the interferential phenomenon. Nowadays, this optical phenomenon is being used, by instance, to determine the thickness and refractive of thin layers by fitting elipsometric measurements to theoretical calculations.[26] In this article we have used the same equations to calculate the reflectance and color of thin layers of Si_3N_4 and PDA on Si. These equations are known as Fresnel coefficients applied to multilayers. The general theory is a variation of the "Transfer Matrix Procedure" and was developed by Abèles, M. Born and Wolf.[27, 28] Basically, the method states that each layer is represented by a 2x2 matrix whose elements depend on the thickness, refractive indices of substrate and layer as well as the incidence angle and polarization state, so that the reflectance of the whole structure, for any incidence or polarization angle, can be deduced from the matrix product of all the layers. Additionally, we have taken into account the possible effect of the surface roughness on the reflectivity assuming a Gaussian profile.[29] The reflectance is modified by a factor ξ as follows ρ, given by:

$$\xi = e^{-\frac{1}{2}\left(\frac{4\pi\cos\theta_i\sigma}{\lambda}\right)} \quad (1)$$

Where σ is the standard deviation of the *z*-hight profile θ_i the incidence angle and λ the wavelength. Although all these calculations are lengthy enough to require the use of a computer, from a qualitatively point of view, the reflectance of a simple structure with a thin layer on a substrate can be visualized by only considering a simple interferential phenomenon [30]. In this sense, when the summation of the optical path of the layers (defined as the product of the thickness times the refractive index) is a semi-integer of the incident wavevector, there is a maximum on the R_s component of the reflectance.

$$\begin{cases} l\dfrac{\pi}{2} = \dfrac{2\pi}{\lambda_0}\sum_j n_j d_j \cos\left(\theta_j\right) & \text{minimum condition} \\ m\pi = \dfrac{2\pi}{\lambda_0}\sum_j n_j d_j \cos\left(\theta_j\right) & \text{maximum condition} \end{cases} \quad (2)$$

Where n_j, d_j and θ_j are respectively the refractive index, thickness and propagation angle corresponding to the *j* layer and *l* and *m* integers. Although criteria of equations (2) can be fulfilled at different incident angles for

a given wavelength, we are only interested into the maximum condition for reflectance according to the human visual perception.

Generally speaking, reflectance depends both on the polarization and on the incidence angle. However, visual perception of color notably simplifies this question. On the one side, visual reflection is seldom verified at normal incidence so that, we need to consider better grazing angles. Moreover, the intensity of the perpendicular component (R_s) increases for larger incident angles, while the parallel component (R_p) tends to cancel around the Brewster condition, which for a Si_3N_4 layer over a Si substrate is satisfied at incidence angles from 60º to 70º. Therefore, it can be concluded that, the color perception can be modeled approximately by the perpendicular polarization component of the reflection at a large incidence angle (θ_i>55º). This feature can be seen in the following Figure 3, where perpendicular and parallel reflections have been calculated for a structure with the same thickness parameters as the 3rd (golden) sample.

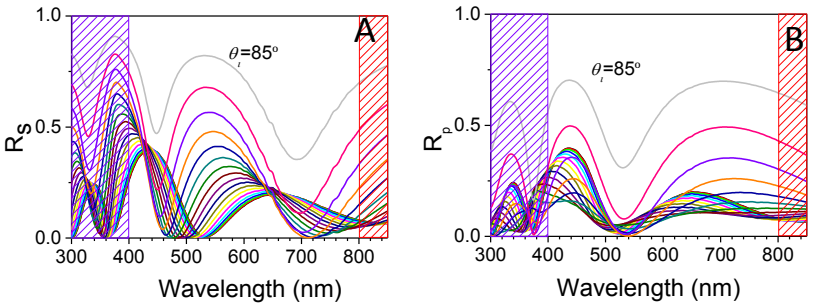

Figure 3. Calculated reflectance spectra of a thin film of PDA of 150 nm over a SSNW (Si_3N_4 thickness of 200 nm), for parallel (R_p) (A) and perpendicular (R_s) (B) components at incidence angles from 0 to 85º.

It is worth to point out that the minima of parallel reflectance at angles close to the Brewster condition nearly coincides with the maxima for the perpendicular polarization. Therefore, we can conclude that for color considerations, only the perpendicular component of the reflectivity needs to be considered. In this sense, the dominant color wavelength is given by the following maximum condition:

$$\lambda_0 = \frac{m}{2}\left[n_{PDA}\, d_{PDA} \cos\left(\arcsin\left(\frac{\sin\theta_i}{n_{PDA}} \right) \right) + n_{Si3N4}\, d_{Si3N4} \cos\left(\arcsin\left(\frac{\sin\theta_i}{n_{Si3N4}} \right) \right) \right] \quad (3)$$

This expression, which is an expansion of equation (2), basically states that the sum of the optical path along both layer (Si_3N_4 substrate and polydopamine (PDA) layer) Where m is the reflection order (m=2 for our samples as it can be seen in the former figure) and θ_i the incidence angle. Although equation (3) introduces a dependence on the incidence angle, in the former figures it can be seen that the reflectance bands do not vary too much for grazing incidence (in particular θ_i >55º). In our case, we have chosen a large incidence angle (θ_i=75º) for experimental considerations.

The experimental values of perpendicular reflectance R_s for the different colored surfaces appear in Figure 4A. Another relevant consideration from equation (3) is that any deposit of PDA of thickness d_{PDA}, will increase the optical path of the whole set, in such manner that the wavelength of the maximum of reflectance, λ_0, will red shift. Because the reflectance maximum is right at the optical region of the spectrum, this multilayer structure becomes very sensitive to any PDA thickness change by the human eye. This predicted trend agrees with the experimental values of R_s of the different samples, since the position of reflectance maximum is notably red-shifted with the number of polymerization cycles.

This approximation (3) can be quite useful to optically determine the thickness deposit of PDA by a simple color inspection, but it includes two non-well characterized parameters, i.e. the Si_3N_4 thickness and the PDA refractive index. Both parameters can be easily determined by spectroscopic ellipsometry. In this sense, we have used an ellipsometry spectrum at an incidence angle of θ_i=75º as well as SEM images on a free PDA sample to determine a value of the Si_3N_4 thickness d_{Si3N4} =208±5 nm.[31] In a similar way, for the determination of the refractive index of PDA, we use a PDA deposit on Si (without the Si_3N_4 deposit) and we take spectra at incidence angles at each 5º from 25 to 75º. Therefore, for each single wavelength we took 11 measurements of the complex value of ρ (coefficient between the parallel and perpendicular reflectance) to determine the real and imaginary part of the refractive index of the PDA plus its thickness. By non-linear least squares fittings using the equations contained in reference 26 we got the spectra of the complex refractive index as they appear on Figure 4B.

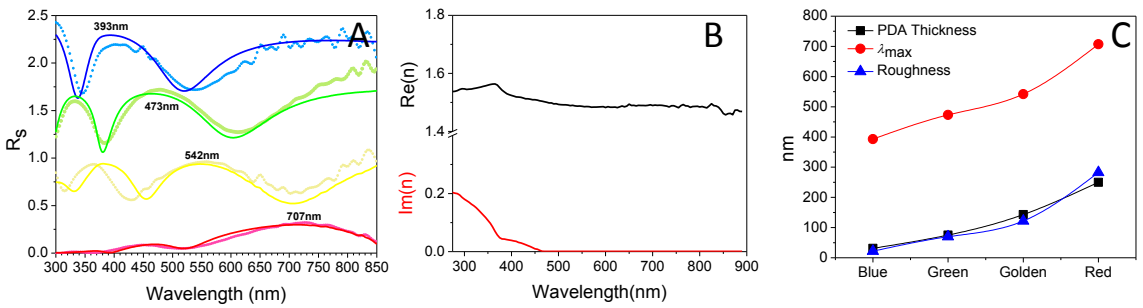

Figure 4. A) Experimental (straight line) and fitted values (dotted) perpendicular reflectance R_s. Each yellow, green and blue curve has been shifted up (for a value of R_s=0.4 each one) for a sake of clarity. B) The real and imaginary part of the refractive index of the PDA as a function of the wavelength. C) Fitted thickness of PDA from ellipsometric measurements (squares), estimated roughness from optical reflectance data (triangles) and maximum of reflectance of the parallel polarization at an incidence angle of 75º (circles).

The estimation of the refractive index of PDA is a question under debate. The obtained values of real part of the refractive index are a 15% smaller than the previously reported by Ming Xiao et al.[18] and Ayaka Kawamura et al.[14] (1.49 against 1.7). It should be noted that both set of measurements were made on colloidal suspensions of PDA in water. However, the herewith obtained value is very close to that of Falk Bernsmann et al.[32] who also used ellipsometry. They reported a value of n= 1.465 at a wavelength of λ=632.8 nm. Therefore, PDA seems to present

different refractive index depending on shape. It may suggest that PDA may change its structure depending on the media they are. It is possible that packing of PDA chains vary from layer to particles. Another possible explanation of these differences, is that scattering based measurements overestimate the real part of the refractive index for slightly absorbing particles, as it the case of PDA. Further research should be made in order to determine if PDA nanoparticles present structural differences with thin layer deposits.

The imaginary part of the refractive index is in good agreement with absorbance data (Supporting Information, Figure S3) showing a transparency regimen up to 500 nm, to them increase its absorbance in three spectral areas, 500 to 380 nm, 380 to 260 nm and below 260 nm.

According to the measured values of the refractive index, the refractive index in the visible range is nearly constant (n~1.49), so that, the imaginary part may be neglected for very thin layers (of a thickness of a few tenths of nm).

Once the refractive index of PDA is known, it is possible to estimate by ellipsometry the thickness of the colored samples. Figure 5 shows the real and imaginary part of the complex reflectance ratio of a blue film PDA over the SSNW measure at 75º. it can be seen the fitting to experimental values of blue sample that leads to PDA thickness determination.

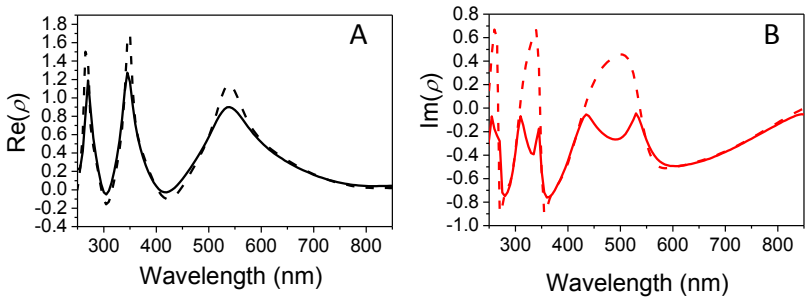

Figure 5. Real (A) and imaginary (B) part of the complex reflectance ratio of a blue film PDA over the SSNW measure at 75º. Continuous line stands for experimental data and dashes for the fitting to determine the PDA thickness. The lack of agreement in the imaginary part of the reflectance ratio around 500 nm may be due to the surface roughness.

The same procedure has been carried out for all the four samples. The thickness values appear in Figure 4C. In this figure a linear correlation between PDA thickness and reflectance maximum seems to appear. Indeed, equation (3) predicts such relationship. Therefore, if we consider that the Si_3N_4 deposit thickness is approximately 200 nm, its refractive index (n_{Si3N4}~2) and that the refractive index of the PDA n_{PDA} ~1.49 we get an approximated expression (assuming an incidence angle of 75º) for λ_0 as λ_0~1.13d_{PDA}+350 nm (fitted expression λ_0=1.39d_{PDA}+354). In this sense, the Si_3N_4 thickness can be perfectly tuned just by the human visual perception as former expression indicates. While the naked Si_3N_4 deposit will present a deep blue color, it can be modified by thin deposits of DPA and the thickness effect can be visually quantified. It should be noted that in the case of the

absence of the Si_3N_4 buffer layer, thicknesses of PDA larger than 170 nm would be required to observe any color effect.[33]

If we compare the thickness of the different samples obtained by optical spectroscopy (figure 4C) with those determined by AFM, we can conclude that there is a good agreement between them. Moreover, both measurement techniques are able to estimate the mean value of roughness, Figure 4C. Again, both sets of data produce similar results. In this case, we have found that roughness seems to be nearly identical to the thickness, which could be the result of precipitation on the surface of PDA clusters previously grown in the suspension. Strategies to minimize nucleation and further precipitation of PDA aggregates in order to get smooth PDA surfaces have been reported.[22] It is well known that roughness tends to reduce reflectance but, with preference, at the high frequency regions introducing a reddish aspect. However, such degree of roughness has a paradoxical effect on color. While for thinner films (blue or green), it does not affect so much, for the thicker ones, roughness blurs nearly totally the 3rd order bands (at higher frequency), in such manner that surface scattering acts as a kind of low frequency pass filter.

Finally, we took advantage of the high color uniformity of the polydopamine film to create color designs in the silicon nitride surface. Figure 6 shows the drawing of a flower on a silicon nitride surface. To do this, a tape covered the silicon nitride surface during the dopamine polymerization while the rest of the surface is exposed to the polymerization medium. Later, the adhesive tape was removed, and the surface was exposed to successive polymerization cycles. The color is red-shifted with the increase of polydopamine thickness. As the number of polymerization cycles increase, the colors of the different areas are controlled with high uniformity.

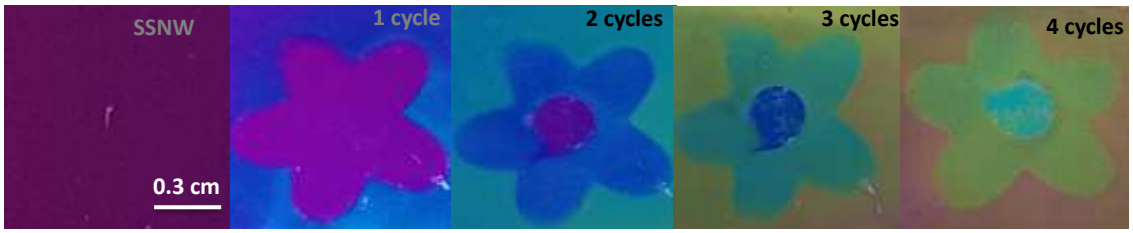

Figure 6. Drawing in silicon nitride surface by coating the surface with polydopamine which presents different thickness in the different patterned areas.

Conclusions

We demonstrate that coating a visible reflective silicon nitride substrate (reflectance band at 400 nm) with a polydopamine film is an outstanding approach to generate surfaces featured with color. Only a very thin film of polydopamine is required to drastically modify the surface reflectance, 30 nm to achieve a blue color and 70 nm to tune the surface green. The color, consequence of the interferential phenomenon, is uniform and easily tunable from blue to red by increasing the polydopamine thickness. This methodology is quite different to the reported in

previous work. [9, 18, 21] It does not precise the assembly of previous synthesized melanin particles, being that the film is grown in situ during the polymerization reaction.

These uniformed surfaces in color and concomitant in thickness were used to determine the refractive index of polydopamine by ellipsometry spectroscopy. The imaginary part of the refractive index is in good agreement with absorbance data showing a transparency regimen up to 500 nm. The refractive index in the visible range is nearly constant (n~1.49), so that, the imaginary part may be neglected for very thin layers. Finally, a linear correlation between PDA thickness and reflectance maximum can be stablished, $\lambda_0 \sim 1.13 d_{PDA}+350$ nm.

Experimental section

The AFM images (5 µm ×5µm) were obtained with a Veeco Multimode scanning probe microscope equipped with a Nanoscope IV a controller operating in tapping mode with a phosphorus doped silicon cantilever (model RTESP). Mean square roughness values were extracted from these images. The software, WSxM 4.0 Beta 8.3,[34] was used for the image analysis. The surface and cross section images were obtained by scanning electron microscopy (SEM) using a Hitachi SU-8000 instrument. Raman spectra were obtained with a Micro Raman Spectometer (LabRAM HR Evolution). Surfaces were excited at 532 nm. Optical characterization: Both, ellipsometric and reflectometric measurements were taken with a GES 5E from SOPRA, provided with a variable angle goniometer, Xe-lamp, monochromator and photomultiplier.

Silicon wafer characteristics

Crystalline silicon wafers with a thickness of 520 µm and coated with a 200 nm layer of silicon nitride (LPCVD) were purchased from Addison Engineering, Inc. The characteristics of the wafer were: i) Front finish: mirror polish, ii) back finish: etch, iii) type: p/Boron and iv) orientation: (100).

Polydopamine coating process

The silicon wafers piece of ca 1 cm × 1 cm was immersed in 30 mL of a buffered solution of dopamine hydrochloride 0.01M. The buffer was trizma-HCl (Sigma-Aldrich) (0.05 M, pH 8.5). The dopamine polymerization was left to proceed at room temperature in an open flask with controlled agitation (200 rpm) for 10 h. After this time, the wafer was washed several times with deionized water and air dried. The surface color after this first cycle was blue. In turn, putting the previously polymerized wafer (blue) in a new dopamine solution for 10 hours turned the sample green. The sample (green) was again washed several times with deionized water and air dried. Yellow color was obtained by repeating the above procedure, to complete a total of 30 hours polymerization. Finally, a fourth polymerization process and subsequent cleaning of the wafer led to red colored surface.

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Keywords: *polydopamine, silicon nitride, color, thin film interference, refractive index*

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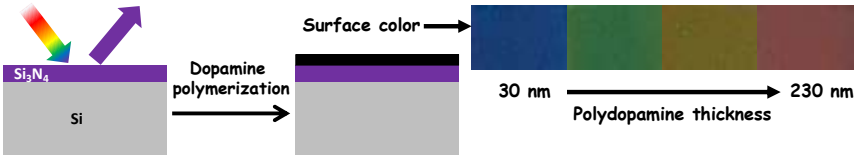

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Polydopamine Color Engineering

A methodology to generate polydopamine surfaces featured with color due to the thin film interference phenomena is reported which is based on depositing ultra-thin films of polydopamine on a Si/Si_3N_4 wafer which exhibits an interferential reflectance maximum right at the visible/UV boundary. Very small film thickness (~30 nm) are enough to notably modify the perceived color. Additionally, good quality of polydopamine deposits allowed the determination of the refractive index of polydopamine by ellipsometry.