In_xAl_{1-x}N chiral nanorods mimicking the polarization features of scarab beetles

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ABSTRACT

The scarab beetle *Cetonia aurata* is known to reflect light with brilliant colors and a high degree of circular polarization. Both color and polarization effects originate from the beetles exoskeleton and have been attributed to a Bragg reflection of the incident light due to a twisted laminar structure. Our strategy for mimicking the optical properties of the *Cetonia aurata* was therefore to design and fabricate transparent, chiral films. A series of films with tailored transparent structures of helicoidal In_xAl_{1-x}N nanorods were grown on sapphire substrates using UHV magnetron sputtering. The value of x is tailored to gradually decrease from one side to the other in each nanorod normal to its growth direction. This introduces an in-plane anisotropy with different refractive indices in the direction of the gradient and perpendicular to it. By rotating the sample during film growth the in-plane optical axis will be rotated from bottom to top and thereby creating a chiral film. Based on Mueller-matrix ellipsometry, optical modeling has been done suggesting that both the exoskeleton of *Cetonia aurata* and our artificial material can be modeled by an anisotropic film made up of a stack of thin layers, each one with its in-plane optical axis slightly rotated with respect to the previous layer. Simulations based on the optical modeling were used to investigate how pitch and thickness of the film together with the optical properties of the constitutive materials affects the width and spectral position of the Bragg reflection band.

Keywords: Mueller-matrix ellipsometry, Nanostructured materials, Chirality, Circular polarization, Beetles

1. INTRODUCTION

Optical properties due to structural phenomena have long been of interest to scientists.¹⁻⁵ Numerous examples of such materials can be found in nature, and especially in the world of insects. With modern technology, materials can be artificially tailored on the nanoscale to mimic such properties. For example many artificial structural colors have been presented by others⁶⁻⁸ who utilize bio-inspired structures. Apart from coloring, there are also many examples of interesting polarizing properties among insects. Pye showed, for instance, that circular polarization is not uncommon in various subfamilies of Hybosoridae and Scarabaeidae beetles.⁹

In this work we have focused on the beetle *Cetonia aurata* of the Scarabaeidae family which has a brilliant metallic sheen and the ability to reflect unpolarized light as almost completely circularly polarized.⁵ The structure of this beetle has been an inspiration to develop advanced nanostructured In_xAl_{1-x}N films which exhibit similar polarization properties. Circular polarizers have many applications in e.g. optical communication or as tunable polarization filters.^{10,11}

The semiconductor material In_xAl_{1-x}N has a high thermal stability and chemical inertness making it suitable for harsh environments. The method of fabrication (briefly described below, and in more detail elsewhere¹²) allows for a high degree of control of the structural properties and tunability of the band gap.

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2. THEORY

Mueller calculus for describing polarization changes is based on Stokes' description of the polarization state of light.¹³ The four Stokes parameters are

$$I = I_x + I_y \quad (1)$$

$$Q = I_x - I_y \quad (2)$$

$$U = I_{+45^\circ} - I_{-45^\circ} \quad (3)$$

$$V = I_r - I_l \quad (4)$$

where I_x , I_y , I_{+45° and I_{-45° represent the irradiance of linearly polarized light at azimuths $0^\circ, 90^\circ, 45^\circ$ and -45° , respectively, with respect to the x-axis in a Cartesian xyz-coordiante system with the light propagating in the z-direction when looking towards the source. I_r and I_l represents the irradiances of right-handed and left-handed circularly polarized light, respectively. The Stokes parameters are often arranged into a vector called the Stokes vector.

When light interacts with a surface, the Stokes vector $\mathbf{S}_i = [I_i, Q_i, U_i, V_i]^T$ of the incoming light is transformed to the Stokes vector of the outgoing light, $\mathbf{S}_o = [I_o, Q_o, U_o, V_o]^T$. This transformation can be expressed as a linear combination of the four Stokes parameters of the incident light. In vector form we have

$$\begin{bmatrix} I_o \\ Q_o \\ U_o \\ V_o \end{bmatrix} = \begin{bmatrix} 1 & m_{12} & m_{13} & m_{14} \\ m_{21} & m_{22} & m_{23} & m_{24} \\ m_{31} & m_{32} & m_{33} & m_{34} \\ m_{41} & m_{42} & m_{43} & m_{44} \end{bmatrix} \begin{bmatrix} 1 \\ Q_i \\ U_i \\ V_i \end{bmatrix} \quad (5)$$

or

$$\mathbf{S}_o = \mathbf{M}\mathbf{S}_i \quad (6)$$

where the Mueller matrix,¹⁴ $\mathbf{M}$, describes the polarization changes that occurred due to the interaction. We use only normalized incident Stokes vectors and Mueller matrices, that is $I_i = 1$ and $m_{11} = 1$, as the absolute reflectance is not studied here. Thereby the Mueller matrix elements are limited to values between -1 and 1 . Measuring the full Mueller matrix gives us the samples response to any polarization state of the incident light. In this case we are only concerned about the samples polarizing properties when illuminated with unpolarized light (e.g. sunlight) which can be described by a Stokes vector as $\mathbf{S}_{u.p.} = [1, 0, 0, 0]^T$. The Stokes vector $\mathbf{S}_o$ of the reflected light in such case can be identified by Eq. 5 in the measured Mueller matrix as $\mathbf{S}_o = [1, m_{21}, m_{31}, m_{41}]^T$.

The degree of polarization of a light beam is calculated from a Stokes vector as¹⁵

$$P = \frac{\sqrt{Q^2 + U^2 + V^2}}{I} \quad (7)$$

For completely polarized light $P = 1$ and then $\sqrt{Q^2 + U^2 + V^2} = I$. For any light beam with less than complete polarization $\sqrt{Q^2 + U^2 + V^2} \leq I$. Here we are studying the materials ability to reflect circularly polarized light and to quantify this we use the degree of circular polarization, P_c , which is calculated as

$$P_c = \frac{\sqrt{V^2}}{I} \quad (8)$$

in case of unpolarized incident light the Mueller-matrix elements may be used directly and Eq. 7 can be written as

$$P = \frac{\sqrt{m_{21}^2 + m_{31}^2 + m_{41}^2}}{I} \quad (9)$$

and Eq. 8 as

$$P_c = m_{41} \quad (10)$$

In Eq. 10 the sign of the Mueller matrix element is kept to show the handedness, where a positive sign stands for right-handed polarization and a negative sign stands for left-handed polarization.

3. EXPERIMENTAL DETAILS

3.1 Instrumentation

The instrument used to measure Mueller matrices in this work is a dual rotating compensator ellipsometer, RC2[®], from J.A. Woollam Co., Inc. The spectral range of the instrument is 245-1700 nm, but we have limited the displayed range to 300-1000 nm to focus on the polarizing effects that occur in the UV-VIS part (between 500 nm and 650 nm for *C. aurata* and between 350 nm and 450 nm for the $\text{In}_x\text{Al}_{1-x}\text{N}$ films.) The incidence angle 20° was used for all experiments. Ideally, normal incidence would have been preferable, but due to instrumental limitations we have used the closest to normal incidence possible. Scanning electron microscopy (SEM) images were taken with a LEO 1550 Gemini (Carl Zeiss, Germany).

3.2 $\text{In}_x\text{Al}_{1-x}\text{N}$ chiral nanorods

The $\text{In}_x\text{Al}_{1-x}\text{N}$ chiral nanorods were grown by ultra-high vacuum magnetron sputter epitaxy on sapphire substrates with a 200 nm TiN bufferlayer. In Fig. 1 an SEM image is shown of the film. The full specifics of

Figure 1. SEM image of a left-handed chiral film of columnar $\text{In}_x\text{Al}_{1-x}\text{N}$ (left) and a schematic visualization of the compositional gradient within each $\text{In}_x\text{Al}_{1-x}\text{N}$ nanorod (right). The gradient is shown only for 1.5 turns whereas the actual samples consist of nominally 5 turns. Blue and red colors refer to InN and AlN, respectively.

the growth mechanism is described elsewhere¹² and only a brief description is given here. With certain growth parameters, a columnar growth is achieved and by co-sputtering with dual sources of Al and In the nucleation starts on the buffer layer with a higher fraction of InN on one side of each nanorod and a higher fraction of AlN on the opposing side. Each nanorod will thus have a compositional gradient which depends on the orientation of the substrate with respect to the In and Al targets during growth. By rotating the sample during growth a helicoidal shape of the gradient throughout the height of each nanorod is achieved. In Fig. 1 a rough sketch is shown with a color gradient representing the compositional gradient within a nanorod. Due to differences in lattice parameters in InN and AlN each atomic layer will be slightly thicker in the In-rich part and thinner in the Al-rich side, and the structure will therefore grow in a curved fashion.¹⁶ Depending on the direction of rotation right- or left-handed chiral films are obtained. In this work the sample was rotated 5 complete turns during growth. Due to screening effects¹⁷ the compositional gradient will cause the material to have different refractive indices parallel to and perpendicular to the gradient. This fact in combination with a columnar growth results in a biaxial anisotropy with two different refractive indices in plane and one out of plane.¹⁸ One sample was prepared for SEM (Fig. 1) and two samples with opposite handedness were used for Mueller-matrix ellipsometry.

Figure 2. Photograph of *Cetonia aurata*

3.3 *Cetonia aurata*

The beetle species analyzed in this paper is *Cetonia aurata* (Linnaeus, 1758), also called rose chafer, of the Scarabaeidae family collected in Sweden and is shown in Fig. 2. The part of the beetle that has been examined is the scutellum which is a small triangular area on the dorsal side of the beetle between the cover wings. It has been suggested that a Bouligand structure¹⁹ is responsible for optical properties such as displayed by *C. aurata* and in Fig. 3 can be seen a cross section SEM image of its cuticle, which is the outer part of the exoskeleton, and a sketch of how a Bouligand structure would fit in with the layered structure. Further information on the structure of *C. aurata* has been published by Arwin et al.²⁰

One specimen was prepared for SEM and a different specimen was used to measure the Mueller matrix using focusing optics reducing the spot size to $<100\ \mu\text{m}$ in diameter.

Figure 3. SEM image of a *Cetonia aurata* cuticle and a schematic description of its layered Bouligand structure

4. RESULTS

4.1 Structural comparison

The cuticle of the beetle *C. aurata* is here assumed to be a twisted layered structure^{20,21} where each layer consists of long parallel formations of chitin. Each layer is rotated with respect to the previous, making the complete structure helicoidal (Fig. 3).

The $\text{In}_x\text{Al}_{1-x}\text{N}$ films consist of a columnar structure where each column forms a spiral.¹² The spirals are randomly distributed over the surface and all spirals are aligned, that is the gradient in each spiral at a certain height (a certain value of z in Fig. 1) has the same orientation throughout the sample. The chirality is thus two-fold with an external, spiral morphology which is due to the curving of the material as it grows, and an internal spiraling gradient in refractive index. However, optical modeling suggests that the internal chirality is

responsible for the optical properties of the film and the external chirality plays a minor role.¹⁸ Optically the $\text{In}_x\text{Al}_{1-x}\text{N}$ films can therefore be described as an effective medium with two different refractive indices in the plane parallel to the surface and one refractive index normal to the surface.

From an optical point of view the two different materials, the cuticle of *C. aurata* and the films of $\text{In}_x\text{Al}_{1-x}\text{N}$ chiral nanorods are thus very similar. Previous results suggest that they can be modeled with, essentially, the same model (cf. Arwin et al.²⁰ and Magnusson et al.¹⁸) with considerations taken for difference in film thicknesses, number of rotations in the helicoidal structures and optical constants. One noticeable feature that separates the $\text{In}_x\text{Al}_{1-x}\text{N}$ spectra from the *C. aurata* spectrum is the presence of oscillations. These oscillations are most likely due to thin film interference in the $\text{In}_x\text{Al}_{1-x}\text{N}$ films. The oscillations are very weak in the *C. aurata* spectrum because of the absorbing and much thicker material. A different beetle, the *Chrysina argenteola*, does exhibit interference oscillations as reported by Arwin et al.^{5,22} These oscillations can also be used to determine the thickness of the cuticle.²³

4.2 Polarizing properties

Figure 4 shows Mueller matrix spectra for *C. aurata* and Figs. 5 and 6 spectra for films of right-handed and

Figure 4. Mueller matrix of the scutellum of a *C. aurata*.

Figure 5. Mueller matrix of a right-handed $\text{In}_x\text{Al}_{1-x}\text{N}$ chiral nanorod film.

left-handed $\text{In}_x\text{Al}_{1-x}\text{N}$ chiral nanorod films, respectively, at an angle of incidence of 20° . The spectral regions of

Figure 6. Mueller matrix of a left-handed $\text{In}_x\text{Al}_{1-x}\text{N}$ chiral nanorod film.

interest here are between 500 nm and 650 nm for the *C. aurata* Mueller matrix and between 350 nm and 450 nm for the $\text{In}_x\text{Al}_{1-x}\text{N}$ Mueller matrices. Outside these regions the matrix elements are more or less constant (except for the oscillations in the $\text{In}_x\text{Al}_{1-x}\text{N}$ spectra discussed in the previous section) and the Mueller matrices bear striking resemblance to that of an isotropic dielectric surface.

In the spectral region of interest two features are noticed: (1) Both materials exhibit strong spectral variation and (2), the Mueller matrix of *C. aurata* differs from the Mueller matrices of the $\text{In}_x\text{Al}_{1-x}\text{N}$ films in that only the diagonal elements and m_{14} and m_{41} show these strong variations.

The first observation can be explained by the structure of the materials. A layered helicoidal structure, such as both the cuticle of *C. aurata* and the $\text{In}_x\text{Al}_{1-x}\text{N}$ films can be approximated by, behaves like a Bragg mirror.²⁴ The second observation can also, at least partially, be explained by the structural properties of the materials. It has been shown²⁰ that the periodicity in the cuticle of *C. aurata* is not perfect, but a certain degree of distribution in the pitch is present, and simulations show that including a distribution in the pitch of the spirals in the $\text{In}_x\text{Al}_{1-x}\text{N}$ films lowers the values of all Mueller matrix elements except the diagonal elements and m_{14} and m_{41} .

The aim of this study was to compare the ability to reflect circularly polarized light between the cuticle of a *C. aurata* beetle and the $\text{In}_x\text{Al}_{1-x}\text{N}$ chiral nanorod films. This is best done by taking a closer look at the degree of circular polarization, P_c described in Eq. 10. In Fig. 7 P_c for all three samples studied are shown. The value

Figure 7. Left: Degree of circular polarization, P_c of *C. aurata*. Right: Degree of circular polarization, P_c of a right-handed $\text{In}_x\text{Al}_{1-x}\text{N}$ chiral nanorod film (blue) and a left-handed $\text{In}_x\text{Al}_{1-x}\text{N}$ chiral nanorod film (red).

of P_c can vary between -1 and 1 , where -1 corresponds to completely left-handed circularly polarized and $+1$ corresponds to completely right-handed circularly polarized light. Both types of materials show high absolute values in P_c , and here we notice the negative values of P_c for *C. aurata* which means that the beetle reflects left-handed near-circularly polarized light, whereas the $\text{In}_x\text{Al}_{1-x}\text{N}$ films reflect left- (right-)handed near-circularly polarized light when the film has left- (right-) handed helicity internally.

5. DISCUSSION

We have here only taken specularly reflected light into account which means that all scattered light is neglected. This might affect the visual aspects of the samples but the polarizing properties in the specularly reflected light is what we are aiming to reproduce. A further limitation to our study is that only normalized Stokes vectors and Mueller matrices have been used which means we have not taken reflectivity into account.

The distribution in pitch of the layered structure of the cuticle of *C. aurata* results in a broadening of the peak in P_c , whereas the pitch of the chiral nanorods in the $\text{In}_x\text{Al}_{1-x}\text{N}$ films is quite well defined and therefore results in a more narrow P_c peak. The secondary peaks surrounding the main feature of the chiral nanorod (seen at 350 nm and 430 nm in the blue spectrum in Fig. 7) spectra are likely the result of a high pitch to thickness ratio.²⁴ A larger film thickness is difficult to achieve due to broadening of the columnar structures as growth progresses and a smaller pitch would shift the peak P_c value further into the UV region of the spectra. This is not of interest to us as one of our future goals is to shift the P_c peak further into the visible region.

ACKNOWLEDGMENTS

Specimen of *C. aurata* were collected by Jan Landin. The SEM image of *C. aurata* was provided by Torun Berlind. This work is supported by grants from the Swedish Research Council and the Knut and Alice Wallenberg Foundation and.

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