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Remarkable crystal and defect structures in butterfly eye nano-nipple arrays

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A B S T R A C T

The corneal nipple structures on the eyes of two nymphalid butterfly species (*Nymphalis antiopa* and *Polygonia interrogationis*) are analyzed in terms of nipple arrangements and associated defects. The nipple arrays in both species have close-packed hexagonal lattices with lattice parameters of about 200 nm. The most abundant defects observed are 5–7 coordination defects that generate dislocations, dislocation-type low angle and structural unit-like high angle grain boundaries, as well as closed-loop defects. These disordered structures are compared with imperfections found in other 2D and 3D crystal structures, and it is concluded that the defects in the nipple arrays are likely not due to random growth accidents. Instead, they could be the result of geometric constraints due to eye curvature or serve a yet undiscovered purpose in the optical properties of these eyes.

1. Introduction

The corneal nipple arrays found on some butterfly, moth and other insect eyes have been studied for several decades (Bernhard and Miller, 1962; Bernhard et al., 1965, 1969; Bernhard, 1967; Gemne, 1971; Wilson and Hutley, 1982; Smith and Butler, 1991; Litinetsky et al., 2002; Watson and Watson, 2004; Stavenga et al., 2006). These structures consist of small cuticular protuberances covering the surface of the eyes with varying degree of regularity in their patterns. Eyes with nipple structure have several advantages over flat eyes (Bernhard et al., 1965; Litinetsky et al., 2002; Stavenga et al., 2006). First, they increase the transmission of light into the eye improving the insect's vision in low-light conditions. This is of particular importance for nocturnal insects such as various moths, explaining why the optical properties associated with such structures are often referred to as the moth-eye effect. However, more recent studies (Kryuchkov et al., 2011; Blagodatski et al., 2014) have shown that antireflective properties also occur in insects that do not live in low-light conditions. Second, the reduced reflection of light from the insect eye provides a certain anti-glare camouflage effect (Stavenga et al., 2006).

Bernhard et al. (1969) classified such arrays on the basis of nipple height (amplitude) into group I (nipples less than 50 nm high), group II (low-sized nipples between 50 and 200 nm in height) and group III (full-sized nipples with heights larger than 200 nm), each group having different antireflection performance due to their physical dimensions. It has been shown that nipples with high aspect ratios and parabolic shapes are more effective in reducing reflection (Stavenga et al., 2006). Such studies formed the basis of the development of artificial moth-eye effect structures, which have already been produced for several years as antireflection surfaces (e.g. Clapham and Hutley, 1973; Wilson and Hutley, 1982; Sawitowski et al., 2004; Huang et al., 2008; Rahman et al., 2015).

As far as the spatial arrangement of nipples is concerned, both irregular and highly ordered arrays have been observed (Kryuchkov et al., 2011; Stavenga et al., 2006; Sergeev et al., 2015). For ordered nipple structures, close packed regions with localized hexagonal structure patterns are observed in various areas on each ommatidium; these regions being referred to as local arrangements of domains (Stavenga et al., 2006). In between these regions are nipple configurations that are different from the structural order found within each domain. However, to date, no study has addressed the details of this peculiar structure in butterfly eyes.

Stemming from the local arrangement of domains, this study hypothesized that there are certain crystallographic principles that govern the formation of the highly ordered corneal nipple structure. The specific aims of the study were twofold. First to analyze the corneal nano-nipple structure of particular butterfly eyes with extremely well-ordered domains using crystallographic principles and identify the associated defect structures. Second, to discuss the potential functional significance of these structures.

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2. Materials and methods

2.1. Sample preparation

Butterfly species used in this study were the Mourning Cloak (*Nymphalis antiopa*) and Question Mark (*Polygonia interrogationis*), both of which belong in the Nymphalidae family. They are similar in size with wingspans of 4–8 cm. Several specimens of each butterfly were received from Thorne's Insect Shoppe located in London, Ontario, Canada. Pictures were taken using a Nikon D3000 Digital Single Lens Reflect (DSLR) Camera. The eyes were separated from their body using a scalpel and a tweezer under an optical stereo microscope.

2.2. Electron microscopy

Scanning electron microscopy (SEM) was the main imaging technique used in the study of nano-nipple structures. In order to perform high-resolution microscopy, a Hitachi S4500 Field Emission SEM was used with 1.5 kV accelerating voltage and a working distance of 5 mm. Imaging was done by capturing secondary electrons. Cathodic arc deposited carbon coatings were applied to prevent charging effects.

3. Results

3.1. Nano-nipple structural analysis

The analysis of nano-nipple structure was carried out on two species in the Nymphalidae family, the Mourning Cloak (*N. antiopa*) and the Question Mark (*P. interrogationis*) butterflies. Fig. 1A shows a low magnification micrograph of a Mourning Cloak butterfly eye. It is covered with many tiny bristles and shows areas of contamination. However, there are also large areas of contamination-free eye structure that were used for microstructural analysis. Fig. 1B shows the regular faceted ommatidia structure of the Mourning Cloak eye with an average corner-to-corner facet size of approximately 27 μm (30 μm for Question Mark). The analyzed facets were not bulged or dented. One of the three facet junctions shows the base of a fractured bristle, indicated by an arrow in Fig. 1B. Fig. 1C shows another junction where three facets are joined together. The nipple structure is clearly visible on each of the facets. An example of such ordered structure is shown in Fig. 1D. The average diameter of nano-nipples in the Mourning Cloak eye is ~170 nm (Fig. 1E) while the Question Mark nano-nipples have an average diameter of ~190 nm (Fig. 1F).

Fig. 2A shows a high magnification micrograph of the interior of a facet on a Question Mark butterfly. From a crystallographic point of view, the structure is a hexagonal primitive (hp) lattice with an average lattice parameter of ~210 nm (~205 nm for Mourning Cloak). The differences in physical dimensions between the two investigated nymphalid butterflies are summarized in Table 1.

The motif in this structure is a single nano-nipple with a base diameter of ~190 nm (~170 nm for Mourning Cloak). This lattice has a hexad rotation axis at each lattice point, which generates diads and triads within the unit cell (Fig. 2B). In addition, there are six mirror lines intersecting each lattice point. The basic crystal structure for their nipple array is therefore the 6 mm point group, with each nipple having 6 nearest neighbours (Fig. 2C). Within each domain this pattern also shows translational symmetry, a prerequisite for a crystalline structure.

However, in addition to the hexagonally close-packed nano-nipple structure, there is an abundance of structural defects that disrupt translational symmetry. This type of defect is associated with a local change in the coordination number from 6 for the perfect hexagonal lattice either to 5 or 7, marked with • and ×, respectively, in the defect region shown in Fig. 2D and E. The differences in coordination are emphasized by the pentagon and the heptagon indicated around the 5 and 7 coordinated defects, respectively. In most cases, the 5 and 7 coordinated defects occur in pairs as shown in Fig. 2F, and they are collectively referred to as a **5–7 defect**. It was observed that the nipples associated with the coordination number of 7 were usually slightly larger than the average nipple size, while the opposite was found for nipples with coordination number 5. This may correlate with the relatively symmetric nipple size distributions observed for both butterflies (Fig. 1E and F).

3.2. Dislocations

The net effect of an isolated 5–7 coordination defect is a lattice distortion very similar to a dislocation in a perfect crystal. An example of lattice distortion can be observed in Fig. 3A by comparing the orientations of unit cells on both sides of the 5–7 defect. In a defect-free crystal, the unit cell orientations are the same at any given location (Fig. 2A). However, in the presence of a 5–7 defect, they are slightly rotated with respect to each other as a result of lattice distortion. Fig. 3B shows the same area with lines tracing the orientation of close-packed nipple rows. Notice the extra row of nano-nipples that terminates at the five-fold coordination defect; this particular structure is analogous to a dislocation in crystallography.

The Burgers circuit is often used to determine the direction and magnitude of lattice displacement due to a dislocation (e.g. Reed-Hill and Abbaschian, 1994). In the nipple arrays, a Burgers circuit is constructed by connecting nano-nipples with 6-fold coordination to form a circuit in the shape of a larger unit cell, in this case a 3 × 3 unit cell. Beginning with zero, the numbers represent the steps required along each edge to complete the circuit. A circuit in a region free of a dislocation/5–7 defect has a perfect rhombic shape (Fig. 3C), and the number of nano-nipples along each side is the same as its parallel counterpart, taking a total of 12 steps to complete the circuit. In contrast, when a Burgers circuit contains a dislocation/5–7 defect (Fig. 3D), an extra step from point 12 to 0 is required to complete the circuit. The extra step represents the lattice distortion caused by the 5–7 defect; its direction and magnitude is regarded as the Burgers vector of the given defect, denoted b in Fig. 3D.

3.3. Grain boundaries and triple junctions

It was further observed that 5–7 coordination defects were not randomly distributed over the facet surface; instead, they were arranged in very specific structures. The sample region of the nano-nipple structure shown in Fig. 4A contains three crystalline domains in different orientations as indicated by the unit cells in Fig. 4B. The domains are divided by rows of 5–7 defects (Fig. 4C), and the degrees of misorientation between domains are indicated along each row of 5–7 defects in Fig. 4D. In this particular arrangement, rows of 5–7 coordination defects effectively constitute defects that are similar to grain boundaries in a crystalline material separating grains (crystals) with different orientations.

In addition, a detailed look at the rows of 5–7 defects revealed an inverse relationship between degrees of misorientation and defect spacing along a boundary. Notice the spacing between 5–7 defects in the boundary with 14° misorientation is much wider than for the row with 33° misorientation in Fig. 4D. Such an inverse relationship between dislocation spacing and lattice misorientation is consistent with the dislocation model, a well known crystallographic model for low-angle grain boundaries (Read and Shockley, 1950).

Fig. 5A is an example of a low-angle boundary in the nano-nipple structure. According to the dislocation model, the degree