Study on structural elementary excitations at semiconductor surfaces and interfaces

Hiroyuki KAGESHIMA
Graduate School of Natural Science and Technology, Shimane University
1060 Nishi-Kawatsucho, Matsue, Shimane 690-8504

In this project, we have been focused on physical properties of structural elementary excitations, such as point defects and precursors, of semiconductor surfaces and interfaces [1, 2, 3]. In this year, we have focused on the physical properties of SiO self-interstitial in SiO_2 [4] and of hBN island on Cu(111) [5]. The calculations were performed based on the first-principles calculation. Program package PHASE/0 was employed [6].

The oxidation of Si is a seemingly simple phenomenon in which Si reacts with O to form Si oxide. However, when one looks at this phenomenon on an atomic scale, an interesting and complex atomic transport phenomenon occurs. O diffuses and moves through the Si oxide film as if it were sewing through the gaps between the atomic bonds of Si and O while maintaining the shape of O_2 molecules. The O_2 decomposes at the interface and breaks into Si atoms to form Si oxide, which induces a large volume expansion and distortion at the interface. The reaction of this distortion causes the Si atoms to move around in the oxide film in a complex manner, resulting in structural deformation of the oxide film and release of the distortion.

The problem is the reaction of this distortion. Roughly speaking, the oxide film seems to be able to deform freely as if it were a gas in a high-temperature environment, but the oxidation temperature is about 700°C to 1000°C, much lower than the melting point of silicon oxide, 1710°C. Therefore, the oxide film should be considered as a solid, and the reaction of strain is thought to induce various defects and set them in motion. The most fundamental of these defects are point defects, and because O is scarce in the oxide film near the interface, O vacancies and interstitial Si are the key points. But considering that compressive stress is applied, interstitial Si is considered to be the most important.

We have been focusing our attention on this point. We have shown from the first-principles calculations that the transport process of interstitial Si in the near-interface oxide film can be constructed by assuming only three fundamental atomic processes (O vacancy transport, Si coordination number conversion, and ACBD bond order conversion). The metastable structures at that time and their energy landscapes are also identified by the first-principles calculations [3]. Finally, the transition structures and barrier heights for each fundamental atomic process are identified [4]. Furthermore, we succeeded in determining the details of the energy landscape of the entire transport process and the maximum barrier height. The values are consistent with the experiment. The climbing image-nudged elastic band method (CI-NEB method) was applied in this calculation.

The hBN growth process on Cu surfaces is also a seemingly simple phenomenon in which B and N precursors aggregate to form hBN islands. However, since this is a binary system of B and N, the shape of the hBN island

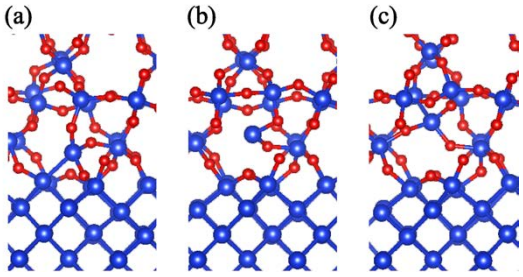

Figure 1: Fundamental processes of Si coordination number conversion. (a) 4-coordinated Si becomes (b) 2-coordinated Si and then returns to (c) 4-coordinated Si.

can change depending on the balance of the number of B and N atoms. The balance between the number of B and N atoms depends on the chemical potential. Therefore, we investigated the relationship between island size, island shape, and chemical potential by the first-principles calculations [5]. Two van der Waals force correction methods, vdwDF2-b86r and D3, were used in the study to confirm the quantitative nature of the relationship.

The basic framework of hBN islands on the Cu surface is the six-membered ring of BN. When the island size is small, only equilateral triangular islands can be formed in principle. However, as the island size increases, equilateral triangular islands are formed only when the chemical potential is extreme, otherwise ribbon-like square islands are formed. Ribbon-shaped islands have both B-only and N-only edges of equal length, which seems to be the origin of the stability of such shaped islands. In fact, the B and N at the edges interact strongly with the Cu substrate, and this interaction may be responsible for the shape of the islands.

These results are interesting when compared to the results for hBN islands that are not on the Cu surface and are completely freestanding. In freestanding islands, islands with B-only edges are unstable and do not form. Moreover, islands in which the six-membered ring is not the basic framework also become stable. In other words, when the interaction between the Cu substrate and the edge atoms of the island is eliminated, the stability and shape of the island become completely foreign.

The importance of the interaction between the edge atoms of the island and the Cu substrate becomes even clearer when looking at the cross-sectional shape of the island: for B-only edges, the distance from the Cu substrate becomes shorter due to the interaction, and the cross-section of the island becomes arched. On the other hand, the N-only edge does not have such a short distance from the Cu substrate, and thus the cross-section of the island is relatively flat. However, the distance to the Cu substrate does not necessarily indicate the strength of the interaction. In fact, when the energy of the edge is evaluated, the N-only edge is more stable than the B-only edge. In other words, the interaction with the Cu substrate is stronger for the N-only edge. This may be related to the fact that N prefers to be more negatively charged and B and Cu prefers to be more positively charged.

References

[1] H. Kageshima, Y. Yajima, K. Shiraishi, and T. Endoh, Jpn. J. Appl. Phys. **58** (2019) 111004 (11 pages).

[2] K. Yata and H. Kageshima, Jpn. J. Appl. Phys., **60** (2021) 035504 (6 pages).

[3] H. Kageshima, T. Akiyama, and K. Shiraishi, Matter. Sci. Semicon. Process. **162** (2023) 107527 (7 pages).

[4] H. Kageshima, T. Akiyama, and K. Shiraishi, Jpn. J. Appl. Phys., 63 (2024) 04SP08 (5 pages).

[5] R. Imamura and H. Kageshima, Jpn. J. Appl. Phys., 63 (2024) 04SP39 (11 pages).

[6] https://azuma.nims.go.jp