γ-Ga$_2$O$_3$ is a metastable form and is transformed to a stable β form at high temperature. However, it might be a more attractive because it has been reported that the metastable γ form shows some unexpected properties; a blue light emission, room temperature ferromagnetism on Mn doping, and selective catalytic reduction of NO in γ-Ga$_2$O$_3$-Al$_2$O$_3$ system. We found a strange structure in γ-Ga$_2$O$_3$ layer grown on an MgO substrate. Many forbidden reflections including both systematic absences and lattice absences were excited in electron diffraction patterns and phase boundaries were observed in atomic column images using high angle annular dark field images.

We proposed a structure model to explain the experimental results. First, cation vacancy ordering is supposed to distort the γ-Ga$_2$O$_3$ crystal lattice. From an ab initio calculation, it is found that the crystal lattice expands along one axis and matches a substrate lattice. Some grains are formed and alter the directions to reduce the distortion for the other axis. Next, it is supposed that the grains are truncated by {110} lattice planes and form rhombic dodecahedrons. The grains are stacked to form honeycomb with {110} phase boundaries. A TEM image and a diffraction pattern simulated by the structure model reproduce the experimental results consistently. The systematic absences are excited by cation vacancy ordering and the lattice absences are excited by double reflections between grains over the phase boundaries.

The rhombic dodecahedral honeycomb structure with cation vacancy ordering is stabilized by the lattice mismatch between the γ-Ga$_2$O$_3$ crystal and the MgO substrate, and it disappears at a depth of 170 nm from the interface.
Fig. 1: A TEM image of γ-Ga$_2$O$_3$ layer grown on an MgO substrate (left) and electron diffraction patterns taken from circled areas (right). Many forbidden reflections are seen in a middle panel of the diffraction patterns.

Fig. 2: An experimental diffraction pattern (left) and a simulated diffraction pattern based on a structure model proposed in this paper. All forbidden reflections are reproduced in the simulated pattern.