In-situ observation of small polarons in Gallium oxide by aberration corrected high resolution transmission electron microscopy

M. Albrecht[1], J. Varley[2], T. Remmele[1], Z.Gałaska[1],R. Uecker[1], C. Van de Walle[2], R.Fornari[1]

1. Leibniz Institute for Crystal Growth, Max-Born-Str. 2, 12489 Berlin, Germany
2. Computational Materials Group, Materials Department, University of California,
Santa Barbara, CA 93106-5050, USA

email.contact.of.corresponding author martin.albrecht@ikz-berlin.de

Keywords: in-situ, atomic defects, aberration corrected TEM

The movement of a carrier in a perfect crystal is goverened by the electronic structure of the material and by the way the carrier polarizes its host. If carrier-lattice copuling is week, this accounted for by an increased effective mass. In case of strong carrier-lattice coupling carriers can be immobilized and selftrap. Such selftrapped carriers, small polarons, move through the lattice by hopping instead of diffusion. Depending on the carrier - lattice coupling these defects can have extremely long live times up to sevreal hours. Selftrapping has been reported for electrons, holes and excitons. It influences a number of physical properties such as electrical and thermal conductivity, specific heat and optical emission. For example in oxides and alkali halides, luminescence is governed by selftrapped excitons, which causes a strong Stokes shift between excitation and emission. Selftrapping may enable defect processes and can be used to intentionally modify materials. Up to now selftrapping of carriers has been evidenced only by indirect measurements, e.g. electron paramagnetic resonance or photoluminescence. Only very recently Rönnow et al. observed by scanning tunneling microscopy of LaSrMnO signatures that were interpreted as polarons localized by some lattice defects. However, since in STM electrons are tunneling into electronic states the signature was quite deloclized and the information hence indirect.

In this paper we present a in-situ study of polaron generation and annihilatio by aberration corrected transmission electron microscopy. The β-Ga_2O_3 single crystals were grown by the Czochralski technique. Samples were prepared by cleaving the crystal. By this technique areas of 100 x 100 nm^2 with a thickness of 2.4 nm and lower could be obatined without ion milling. Thus we have no amorphous surface layers, that induce disturbing constrast fluctuatons that would hamper the analysis single atomic defects. The TEM studies were performed in a Titan 80-300 microscope operating at 300 kV equipped with a spherical aberration corrector for imaging lens. Images were recorded with an FEI EAGLE 2kx2k CCD. Polarons were excited by inelastic scattering of electrons in these samples. The structure of the three different hole polarons were claculated by hybrid functions.

Fig. 1a shows the most stable polaron, a hole bound to oxygen (III) in the monoclinc unit cell of β-Ga_2O_3. Bonding of the hole to the oxygen atom leads to a bond breaking of the Ga atom and in turn to a strong lattice relaxation. The Ga atom moves by 0.1nm from its equilibrium position. This movement could in principle be observed in both, the 101 and the 010 projection, however, since cleavage of the sample ist most easy in the c-plane, we used the 101 projection. To define optimized imaging conditions (c_s and defocus) for polaron detection we performed contrast simulation model based on the ab-initio models. We found that for this special system a negative c_s of -5µm and a slighlty positive defocus is optimum as can be seen in Fig. 2. These conditions provide for an enhanced Ga column contrast, but keep the oxygen column contrast as low as possible, which results in optimum contrast of the polaron. We then took series of typically 30 images with 0.2-0.4s recording time each. To detect the polaron we cross-correlated the images, averaged them and substratcted the averaged image from each single image. Thus the periodic background in the image is removed and the polaron, if present, can be located. Fig. 1b shows the comparison of a contrast simulation and experimenatl image of sample that has a thickness of 2 unit cells, which are in ecellent agreement. Formation, recombination and transfer processes of single selftrapped holes could be revealed in real time. Typpically we find the lifetime of the polaron to be in the range of several seconds. We compare these observations with ab-initio calculations on the hole transfer process. Our analysis shows that aberration corrected TEM may reveal atomic defects, charge transfer and lattice relaxation processes in situ.

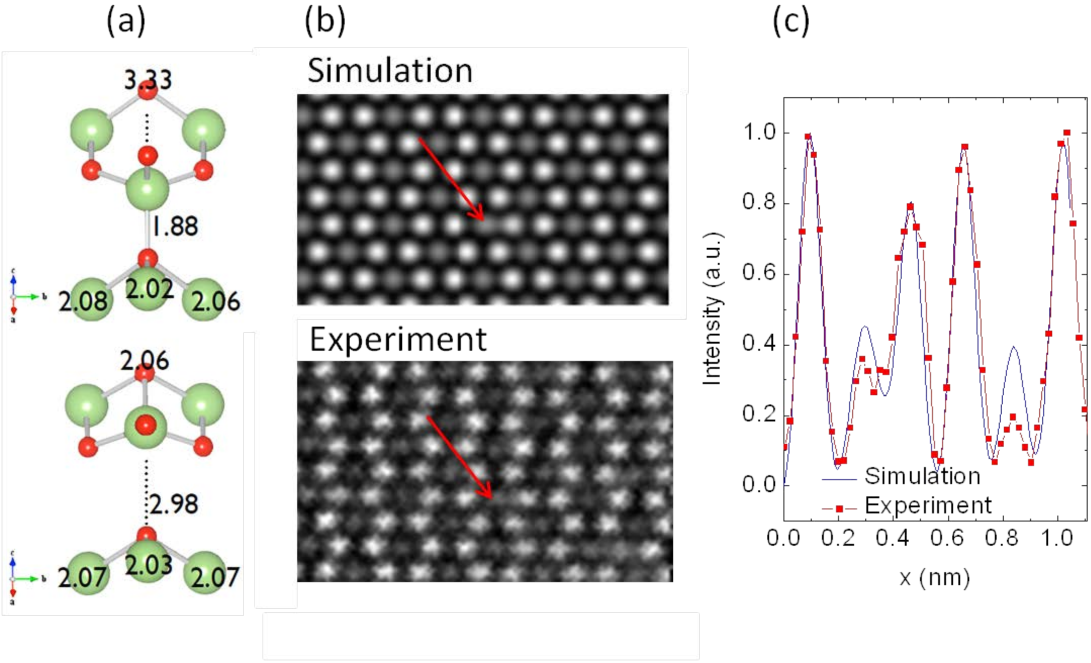

Figure 1: (a) Structural model of a polaron in Ga_2O_3. Oxygen atoms are red, Ga atoms are green. Upper model shows the pristine crystal, the lower the polaron. The Ga atom is shifted by 0.11nm. (b) The comparison between simulated and experimental contrast of a polaron in 101 projection shows an excellent agreement between experiment and simulation. (c) Comparison of line scans taken at the simulated and experimental image.

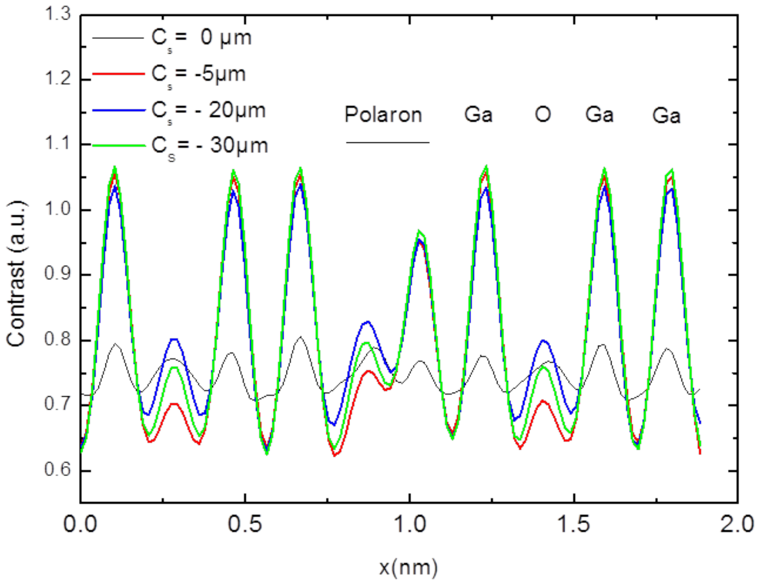

Figure 2*: Contrast simulations of polarons as dependent on spherical aberration. The contrast is optimized at a slightly negative c_s of 5 µm.*