Electron beam effects on metal and semiconductor oxide films - structure and electrical properties

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In situ TEM techniques provide valuable information on structure-property correlations to understand the behavior of materials at the nanoscale. However, one of the critical issues in interpreting *in situ* experiments are effects due to the physical dimensions of the sample and especially due to the interaction with the electron beam. While electron beam damage is well known to be critical e.g. in *in situ* battery studies, both due to the lithium compounds as well as due to the typical organic electrolytes used, it is typically not considered in detail when working with metal or semiconductor oxides. However, depending on the properties of interest, even small structural changes induced by the electron beam at fairly low dose can significantly alter the behavior of the material.

With this work, we have been focusing on the electrical properties of metal and semiconductor oxides, which are used e.g. in memristive devices [1]. These devices typically work on the principle of valance change memories where migration of oxygen anions and vacancies result in local redox reactions creating pathways for higher conductivity (low resistive state) and vice versa for lower conductivity (high resistive state). Experimentally demanding *in situ* and *ex situ* studies are aiming at understanding the structural and resistive changes used to realize the binary or multinary switching behavior.

However, while the structural changes due to the electron beam are often difficult to identify clearly, especially if the oxides are amorphous, the electrical response can be drastic even at fairly low dose, both, at low and high TEM operation voltage. Figure 1 illustrates the resistance change of a thin SiO_2 film from an insulator to a semiconductor due electron beam illumination with a dose of ~$3*10^7$ e/nm^2. The change in conductivity seems to be related to the formation of silicon rich quantum dots due to an electron beam induced reduction (Figure 2) [2]. The conductivity change is reversible by exposure to air, further supporting the idea of electron beam induced reduction as the source of the conductivity changes. Further details on the dose and high-tension dependence of the electrical thin film properties as well as the reversibility of the changes will be discussed in this presentation for SiO_2 thin films as well as different metal oxide films, which are even more electron beam sensitive exhibiting significant changes at doses as low as ~10^4 e/nm^2. These changes would drastically modify any *in situ* electrical device measurements and have to be carefully considered during *in situ* experiments both in the SEM and the TEM.

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References

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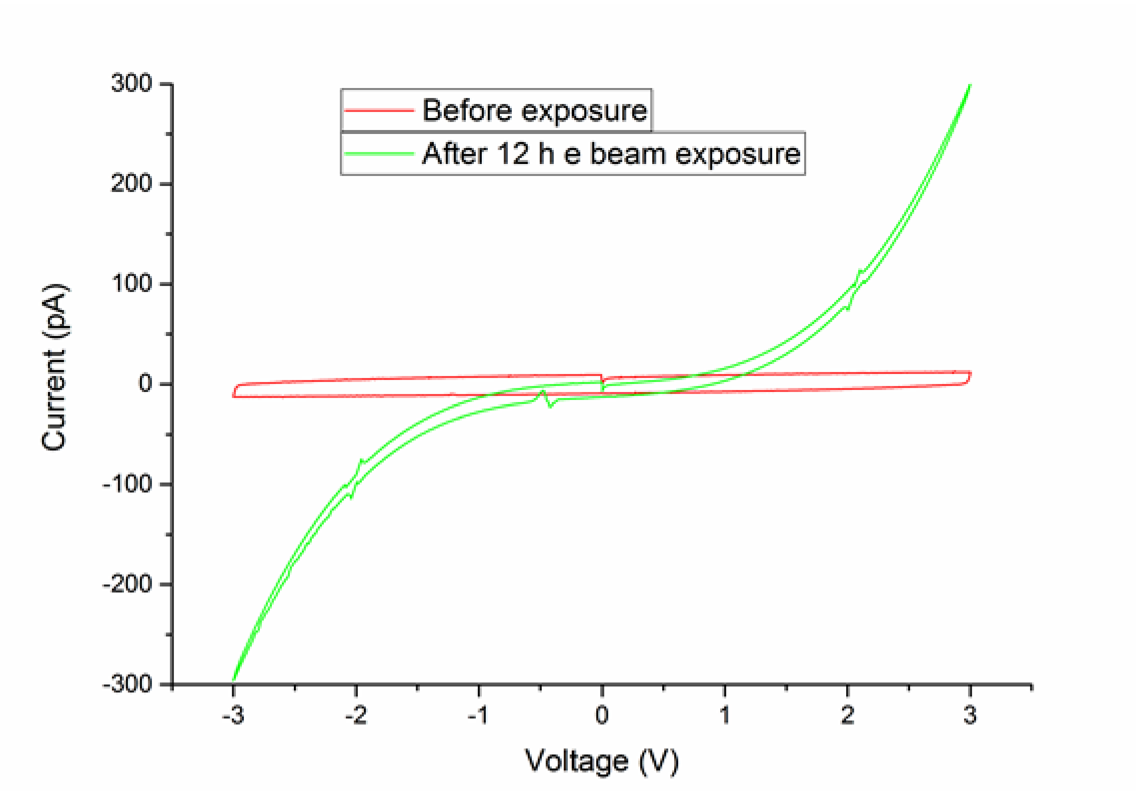

Figure 1: Electrical conductivity of a 15 nm thick SiO_2 thin film before and after exposure to the electron beam with a total dose of $3*10^7$ e/nm^2. The I/V curves were recorded with the electron beam off. Dose rate ~500 e/nm^2.s.

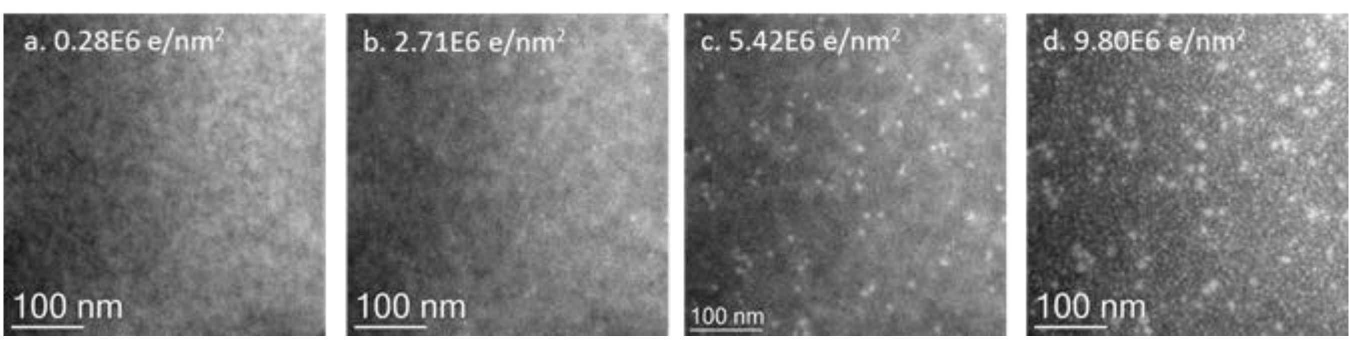

Figure 2: EFTEM images obtained at an energy loss of 17 eV showing the Si nanoparticle formation. Dose rate: ~ 55000 e/nm^2.s.