Spatially Resolved Electron Energy-Loss Spectroscopy, a Tool to Verify Electronic Structure Calculations in Nanostructured Materials

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ABSTRACT

Modern mcroscopy allows a direct comparison between experimental results and the atomic and electronic structure as obtained by state of the art ab-initio calculations. The phase reconstruction technique allows one to determine the positions of atomic columns with an accuracy of about 30pm. The atomic structure can be studied directly (without computer simulation or reconstruction) with Z-contrast imaging and contains the atomic structure. The electronic structure with atomic column spatial resolution can be determined with spatially–resolved electron energy–loss spectroscopy.

We will show that the atomic calculations and micrographs of a copper doped aluminum grain boundary agrees within the errors of theory and experiments (30pm). The electronic structure as determined by EELS and by density functional theory agrees well enough to apply this combination to the Si/SiO2 interface and determine the structure of this complicated heterogeneous interface.

Keywords: Z-contrast imaging, TEM, EELS, Si/SiO_2, DOS

1 Introduction

The combination of theoretical and experimental investigations allows a deeper insight into the materials than the sum of its parts. This synergetic relationship allows us to exclude artefacts and to understand even complicated structures. To achieve this all methods used must have the same spatial resolution. As ab initio theory can only handle a few atoms, the experiments must be performed with atomic resolution. Naturally, electron microscopes can provide images of the atomic structure. However, the electronic and chemical structure also can be probed now with transmission electron microscopes at atomic spatial resolution und progress has been made in th eimaging mehtods themselves.

In this paper we will introduce these novel imaging and analytical techniques with their capabilities. We will show some examples where the combination of these experimental techniques with theoretical calculation allowed a deeper understand of material interfaces. Especially we will report the advances in our understanding of the atomic and electronic structure of the Si/SiO_2 interface.

2 Methods

In this section we will briefly introduce the experimental and theoretical methods used. Their interaction will be made clear in the results chapter, below. Note that these results were not obtained with a spherical aberration corrector for magnetic (objective) lenses, which were available only very recently. This corrector will enable us to obtain the exceptional results shown here on a day to day basis.

2.1 Experimental methods

Phase Reconstruction
For phase reconstruction, a focus series of conventional high resolution transition microscopy (HRTEM) images has to be obtained. The numerical reconstruction or restoration of the properly phased scattered electron beams was carried out with the Philips Brite Euram focal series reconstruction package The usual limitation of HRTEM is that the atomic structure can not be obtained directly, because the image is formed by the interference of elastically scattered waves. Thus, we may consider the HRTEM image as a hologram, which cannot be interpreted naively. The phase reconstruction method allows one to calculate the exit wave of the object, and therefore the atomic structure directly. This method has the advantage that the atomic position can be determined very accurately. The information limit at the TEM at the NCEM is better than 100 pm and the absolute atom positions can be determined to about 30 pm.

Z-contrast Imaging
In contrast to the HRTEM or phase reconstruction method, a Z-contrast image is acquired serially pixel for pixel, as a focused beam is scanned over a rectangular area (figure 1). Because of slight sample drift, the atomic positions cannot be determined as accurately as with a parallel detection method. However, Z-contrast imaging provides a variety of advantages over those other imaging methods. In a Z-contrast image, the image is formed by electrons scattered to high angles (> 25 mrad). These

electrons are scattered incoherently and therefore the spatial resolution is enhanced. The images are also directly interpretable, since the intensity is increased only when the electron probe hits an atomic column . The electron beam remains focused at the atomic column or in between, due to the (coherent) channeling effect.

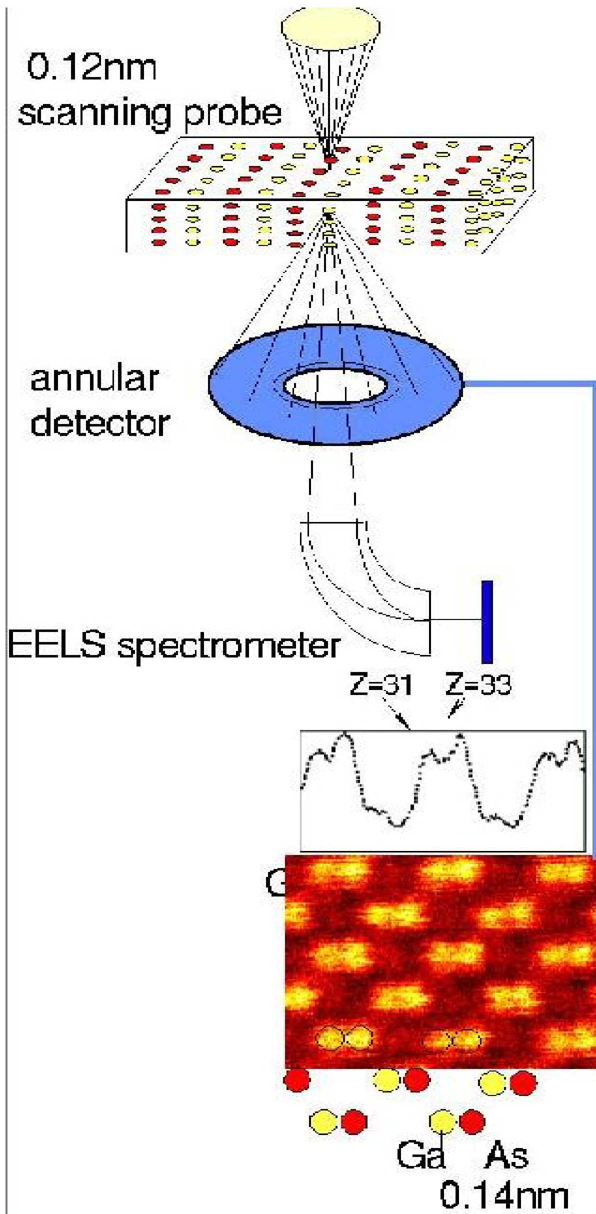

Figure 1: Schematic representation of Z–contrast imaging

Rutherford scattering describes the electrons which are detected by the high angle annular detector, and thus the intensity is proportional to the square of the mean atomic number of the probed volume (for example a single atomic column in a crystal). Figure 1 shows a micrograph of GaAs, where we can distinguish the two elements by an intensity profile. The point resolution is given by the FWHM of the probe profile diameter, which is 130 pm in the case of the 300kV dedicated scanning TEM (STEM) VG HB603 U. Another advantage of this method is that it can be used simultaneously with electron energy–loss spectroscopy (EELS), which uses only electrons scattered to rather low angles (as seen in figure 1).

Electron Energy–Loss Spectroscopy We concentrate here on the core-losses of an electron energy-loss spectrum (EELS), which contains the chemical and electronic structure information, while we ignore all the dielectric function information which is accessible in the low-loss part of an EELS spectrum. The fast electrons in the STEM (or TEM) can excite a core electron above the Fermi level, and loose a certain energy. This energy–loss is detected in an EELS, where a magnetic field acts as a prism. The area under the so–called ionization edge weighted by the cross section of the elements allows the quantification of the chemical composition. The shape of these ionization edges reflects the density of states with some excitonic contribution from the core hole that is created in this inelastic scattering process. This electronic structure can be readily calculated by modern density functional theories. The spatial resolution of this analytic TEM method is comparable to the one in Z-contrast imaging [1].

2.2 Theoretical Methods

Z-contrast images serve as input for our atomic structure calculations, since the structure is determined model independent. This start configuration is relaxed with a plane wave, pseudopotential method in local density approximation. This method is more efficient for this task than an all-electron method, which we need for the electronic structure calculations to include localized excitonic effects.We are using a full–potential linearized augmented plane wave method, where we can include a core hole explicitely. Note that this calculations have to be done with rather large supercells ($>$ 60 atoms), where the excited atoms are separated sufficiently.

3 Results

In the following examples will demonstrate how well experiment and theory can agree. Only with a combination of these synergetic methods was it possible to achieve in–depth understanding understanding of these materials.

3.1 Atomic Structure Determination: Al Grain Boundary

We investigated a $\Sigma 5$ Al grain boundary with the phase reconstruction method to determine the atomic positions and with the Z-contrast method to establish

to which atomic site the copper segregates (figure 2). The Z–contrast image shows that Cu segregates to an interstitial site, normally not occupied in fcc metal tilt boundaries, which have all the same atomic structure. Careful examination of the images shows that two grain boundary configurations exist. The structural unit at the right of image 2 posseses two atomic column, while one atomic column is present in the structural units on the left.

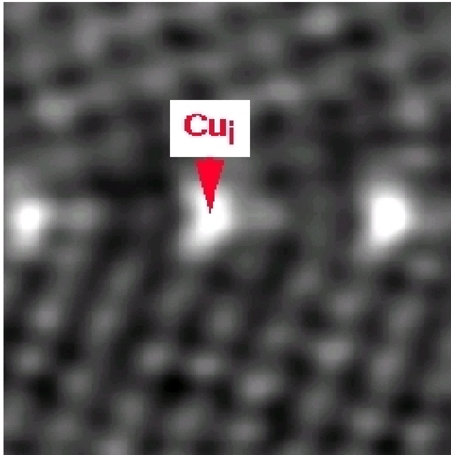

Figure 2: Z-contrast image of an Al grain boundary with Cu segregated to special sites in the grain boundary, which are seen as bright spots, due to chemical sensitivity

This result serves as an input for ab–initio calculations with a plane-wave/pseudopotential method in local density approximation. After relaxation, the theoretical and experimental results were compared. We want to stress that these results were obtained independently.

The level of agreement between theory and experiment is stunning, as can be seen in figure 3, where we show the results of one of the two observed configurations. The test of other grain boundary structures with and without copper at various positions shows clearly that there are only two atomic configurations with low energies, the ones observed.

3.2 Electronic Structure Determination: Semiconductors and Insulators

In this section we want to demonstrate that the energy–loss near–edge fine structure (ELNES) of an ionization edge in an EELS spectrum can be successfully extracted from the electronic structure calculations. The application of these methods to an interface, which demonstrates the spatial resolution of these methods, will be discussed in the following section.

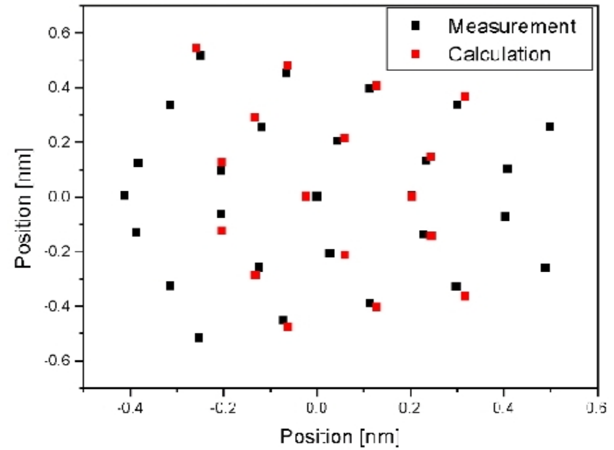

Figure 3: Comparison of the experimental and the theoretical atom positions at a Al grain boundary doped with Cu.

The Si-L_3 edge [3] will serve here as an example for a variety of materials (SiO_2, MgO, ...)[4] , which we will show in the presentation.

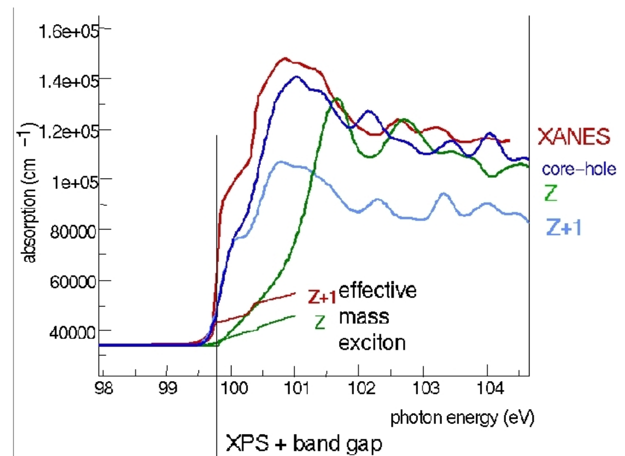

Figure 4: Comparison of the experimental and various simulated Si-L_3 ionization edges.

As we see in figure 4, the explicit core hole inclusion in the all-electron calculation, correctly yields not only the shape of the absorption edge, but also the height. The steep rise of the experimental edge cannot be reproduced as accurately, but reproduction was greatly improved by the usage of the large super cells used here; an even larger supercell is expected to give even better agreement.Undeniably the localized excitonic effects must be included in the ELNES simulation. A first test of the influence of the excitons on an ELNES (or XANES) can be made by comparing the location of the edge with an experimental value (the distance from the core states to the valence band maximum from XPS; and

the band gap from optical absoroption experiments). If there is no excitonic effect, this will be the start of the unocupied DOS. We calculated the changes of the edge onset with an all-electron calculation (a subtraction of the total energy of a supercell with an excited atom and a supercell in ground state), which results to an agreement with experiment better than 1% in all the investigated systems[4]. We conclude that we can simulate the ELNES successfully with the inclusion of excitonic effects.

3.3 The Si/SiO_2 Interface

Since the Z-contrast image allows one to investigate the atomic structure of crystalline material, we learn from the Z-contrast image in figure 4 that the oxide is amorphous right up to the atomically sharp silicon. With a variation of the inner angle of the HAADF detector, we can study the stress at these interfaces; but no stress was detectable at this Si/SiO_2 interface.

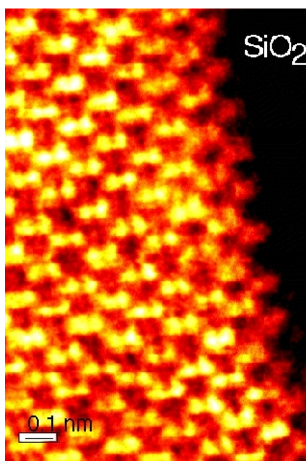

Figure 5: A atomic resolution Z-contrast image of an Si/SiO_2 interface

Since we were interested in the atomistic structure of the Si/SiO_2 interface, we employed the combination of EELS and density functional theory. EELS is not dependent on a crystalline structure even though the spatial resolution is slightly reduced in amorphous materials. Many different structures were calculated in this study, and the results showed that a chemical abrupt interface is energetically preferred.

However a comparison between the simulated spectra in figure 5 with our EELS spectra results in the statement that the thermally grown interface investigated here has a silicon rich oxide layer of about 0.3 nm, which is consistent with earlier findings. We want to note (and will show in the presentation) that our simulations show that the oxygen K edge is not suitable for an extraction of the atomic structure of the Si/SiO_2 interface.

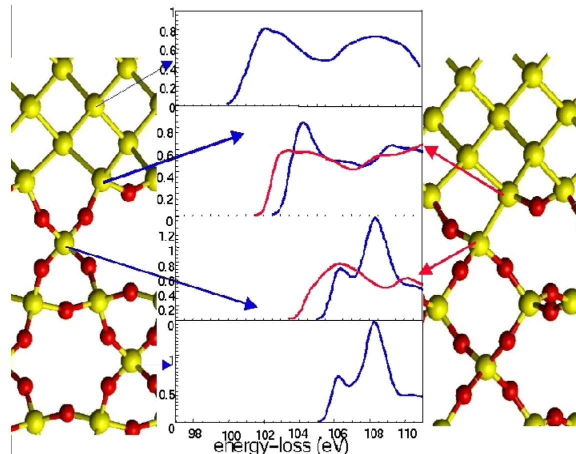

Figure 6: Simulation of Si-L_3 ionization edges at the Si/SiO_2 interface

face. Furthermore, we calculated the relative bandgap changes across the interface and found that an abrupt interface has an extremely sharp transition (< 0.2nm) between the Si and the SiO_2 band gap, while the suboxide band gap needs a transition region of more than 0.6nm. Therefore a transistor with a gate oxide thickness of 1.2 nm (which was already demonstrated), would not work with an interface of such an atomic structure. Investigations such as those shown here will clarify the atomic structure of modern gate oxides and also can be transferred to high-K dielectrics.

4 Conclusion

In this paper we demonstrated that the combination of modern microscopy and theoretical calculations can lead to a deeper understanding of complex interfaces. The atomic and electronic structure can be determined through a combination of theoretical and experimental methods, and when both agree to the level shown here, the interpretation of the results is easier and more reliable than ever before. Fast characterization and the understanding that is the basis for predictive materials design will result from investigations like those shown here.

REFERENCES

[1] Duscher, G., N. D. Browning and S. J. Pennycook: phys. stat .sol. (a), 166:327-342, 1998.

[2] J.Plitzko, G.Duscher, and C.Kieselovski; submitted

[3] Buzcko R., G. Duscher, S. J. Pennycook, and S. T. Panteli Phys. Rev. Lett. 85: 2168-2171, 2000.

[4] Duscher, G., R. Buzcko, S. J. Pennycook, and S. T. Pante Ultramicroscopy, 86: 355-362, 2001.