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Valence EELS below the limit of inelastic delocalization using conical dark field EFTEM or Bessel beams

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ABSTRACT

In this experimental work we present novel methods to increase the spatial resolution of valence electron energy loss spectrometry (VEELS) investigations below the limit given by the inelastic delocalization. For this purpose we analyse a layer stack consisting of silicon/silicon-oxide/silicon-nitride/silicon-oxide/silicon (SONOS) with varying layer thickness down to the 2 nm level. Using a combination of a conical illumination and energy filtered transmission electron microscopy we are able to identify the layers by using low energy losses. Employing Bessel beams we demonstrate that VEELS can be performed in dark-field conditions while simultaneously the Bessel beam increases the spatial resolution of the elastic image due to less sensitivity to the spherical aberration of the condenser lens system. The dark-field conditions also guarantee that only electrons are collected that have neither undergone an energy loss being due to the Čerenkov effect, nor due to the excitation of transition radiation or light guiding modes. We consequently are able to measure the optical properties of a 2.5 nm thin oxide being sandwiched by the silicon substrate and a silicon-nitride layer.

1. Introduction

The determination of optical properties of thin buried structures, like quantum wells and gate oxide layers, still remains an unsolved problem in optical spectroscopy as well as in electron spectrometry. Whereas in optical spectroscopy one is spatially limited to dimensions of approximately half the wavelength of light, electron spectrometry is limited by the Coulomb interaction between the electron probe and the valence electrons of the specimen. The long-range nature of this electrostatic force imposes a basic limit on the spatial resolution of electron spectrometry. It is called the “inelastic delocalization” and depends on the investigated energy transfer, as indicated by the Bohr impact parameter $b = \hbar v/\Delta E$ for electrons of velocity v [1]. A small b implies a strong force and large scattering angles, so scattering should appear more localized when being observed in darkfield conditions [2,3]. This knowledge was already applied by using an in-column energy filter for recording energy filtered annular dark-field scanning transmission electron microscopy (EF-STEM) images [4].

Besides the problem of the inelastic delocalization another drawback appears as soon as high electron energies are used: the excitation of Čerenkov losses which are altering the valence electron energy loss (VEELS) spectrum [5,6]. Čerenkov losses are excited as soon as the speed of the swift probe electron exceeds the speed of light inside the medium and $\beta^2\varepsilon(\omega) > 1$, with $\omega = \Delta E/\hbar$ and β as v/c_0. Lowering the beam energy can be an alternative, but for a scanning transmission electron microscope (STEM) without an aberration corrector this means that the electron probe cannot be focussed sufficiently in order to study layers of a thickness below approximately five nanometres [7]. Due to the fact that the excitation of Čerenkov radiation causes only small energy losses, scattering angles $\vartheta < 1$ mrad can be observed. A way out of this dilemma would be to use dark-field conditions, with scattering angles being larger than the maximum Čerenkov scattering angle of the respective material.

As a consequence, it seems as if dark-field VEELS is the solution for both above-mentioned problems. But this is only correct under very restricted conditions, e.g. the investigated material has to have very flat energy bands. This is the case for silicon oxide as well as for silicon nitride, but not for silicon or most other semiconducting materials. So for an earlier investigated structure – InGaN quantum wells in a GaN matrix [7] – dark-field VEELS is not a practicable method. The resulting dark-field VEELS spectra would not be related to the optical energy loss function $\Im(-1/\varepsilon(\omega, \vec{q} = 0))$, because $\vec{q} \neq 0$ in darkfield conditions.

Therefore the manuscript is structured as follows: Section 2 gives a brief overview on the physical limits being posed by inelastic delocalization and the achievable spatial resolution in VEELS when working

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in dark-field conditions, followed by a short introduction into the excitation of Čerenkov losses. Section 3 discusses experimental details and introduces the test specimen: a SONOS transistor. We discuss its layer structure, layer dimensions and chemistry. Section 4 deals with the application of conical darkfield energy filtered transmission electron microscopy (conDF-EFTEM) and Section 5 explains the production and usage of Bessel beams in STEM for dark-field VEELS applications. Finally we discuss the results with respect to future applications for the analysis of low dimensional buried structures. For this purpose the band structure of silicon, silicon oxide and silicon nitride is addressed.

2. Physical limitations

2.1. The inelastic delocalization

The discussion about non-locality dates back to the 1930s, when Einstein and Bohr proposed the light-box *Gedankenexperiment* [8]. As a consequence a wide discussion about non-locality in inelastic electron scattering followed [9–12] and is reviewed here only briefly. Looking back to Bohr's impact parameter b

$$b = \frac{2\pi\hbar v}{\Delta E}$$

with v as the speed of the swift probe electron passing by the specimen at a distance b and losing an energy ΔE, one directly sees that the non-locality is inverse proportional to the energy loss ΔE. The development of dielectric excitation theory has improved and leads to a more realistic description of the delocalization [11,13]. In slab like specimens having a planar interface between materials A and B oriented parallel to the electron beam axis with the electron trajectory at a distance b from the interface inside material B, the differential inelastic scattering probability $dP(b, \omega)$ per unit energy loss $d(\hbar\omega)$ is given by

$$\frac{dP(b,\omega)}{d(\hbar\omega)} = \frac{e^2}{2\pi\varepsilon_0\hbar^2 v^2}\left(\Im\left\{\frac{-1}{\varepsilon_B}\right\}\ln\left(\frac{q_c v}{\omega}\right) + K_0\left(\frac{2b\omega}{v}\right)\left[\Im\left\{\frac{-2}{\varepsilon_A(\omega)+\varepsilon_B(\omega)}\right\} - \Im\left\{\frac{-1}{\varepsilon_B(\omega)}\right\}\right]\right). \quad (1)$$

Eq. (1) also includes the dielectric damping of material A. Nonetheless, as long as the scattering angle, at which the spectrometer is located, is kept less small or close to zero, one sees – on the inter atomic distance scale – a rather delocalized low loss signal. In order to improve the localization one has two possibilities. First, one can reduce the energy of the probe electron, or, second, one can measure the inelastic signal at larger momentum transfer. This can also be understood in terms of Heisenberg's uncertainty principle

$$\Delta x \Delta p \geq \hbar/2 \quad (2)$$

meaning, the smaller the uncertainty in space Δx, the larger must be the uncertainty in momentum transfer. Such an experimental set-up can be obtained by measuring under darkfield conditions [12], because the variance of q depicts Δp in Eq. (2) in darkfield conditions, where many different q-vectors enter the spectrometer.

2.2. Čerenkov losses and retardation effects

The second physical limitation for quantitative VEELS at high spatial resolution is the excitation of Čerenkov losses, transition radiation losses (TRL) and light guiding modes (LGM). All these losses alter the VEELS spectrum and so were the topic of profound discussion [5,14]. As a result, a few experimental solutions were presented [6], like the difference method [15] or a reduction of the beam energy [16], to circumvent this physical limitation. The acquired VEELS data is then applicable for Kramers–Kronig Analysis (KKA). Although the reduction of beam energy reduces or even totally eliminates the excitation of

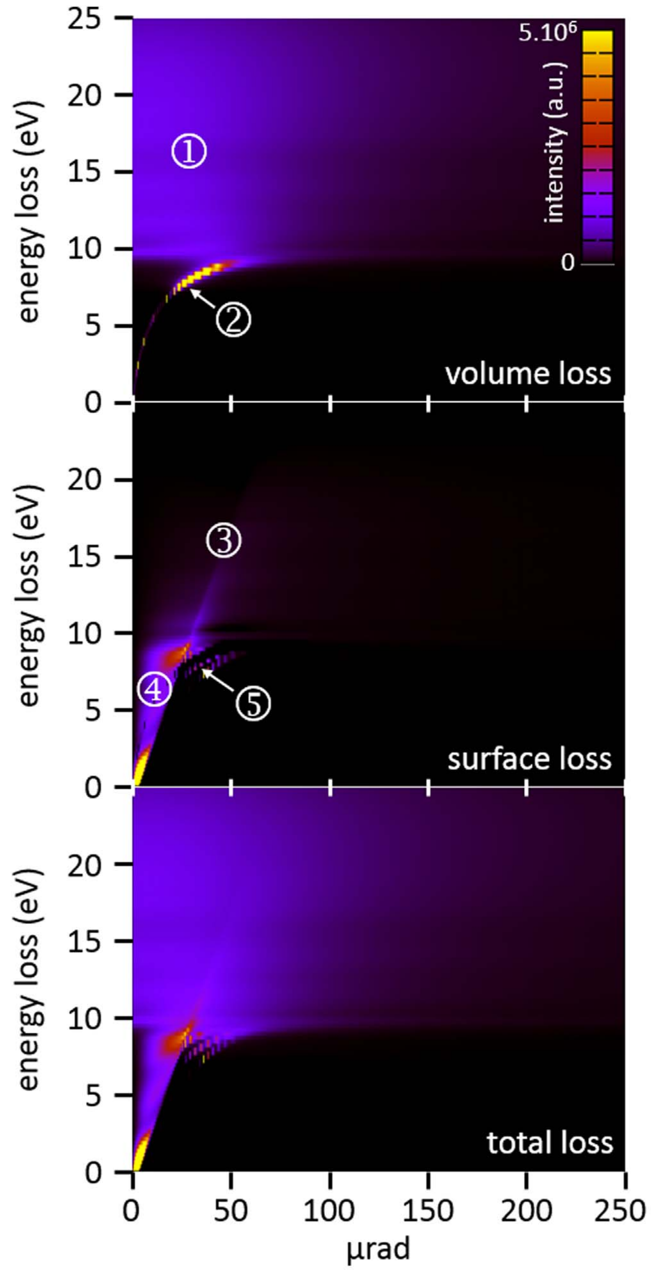

Fig. 1. E–q maps of 100 nm thick SiO_2 for 200 keV electrons showing on top the volume losses, in the middle the surface losses, and at the bottom the total loss (being the sum of the volume and surface losses): (1) interband transitions and volume plasmon, (2) Čerenkov loss, (3) light line, (4) transition radiation loss (TRL), (5) light guiding modes (LGM).

Čerenkov losses, the imaging performance of an uncorrected TEM is also reduced. Additionally, other retardation effects and guiding light modes could alter the VEELS spectrum even if the speed of the probe electron is below the Čerenkov limit v_c, which is

$$v_c = \frac{c_0}{n}$$

with c_0 as the vacuum speed of light and n as the refractive index of the specimen [17]. TRL and LGM are excited at beam energies even below the Čerenkov limit. In order to get a sound picture of the relativistic energy losses, we calculated their angular distribution up to $\Delta E = 25$ eV energy loss and 250 µrad scattering angles as E–q diagrams (Fig. 1) for 200 keV electrons passing through a 100 nm thick foil of SiO_2. When looking at the volume losses only, the interband transitions and volume plasmon loss (1) besides the dispersion of the Čerenkov loss (2) up to a