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Ultramicroscopy 108 (2008) 270–276
ultramicroscopy
www.elsevier.com/locate/ultramic

Prospects for analyzing the electronic properties in nanoscale systems by VEELS

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Abstract

Valence electron energy-loss spectroscopy in the scanning transmission electron microscope can provide detailed information on the electronic structure of individual nanostructures. By employing the latest advances in electron optical devices, such as a probe aberration corrector and an electron monochromator, the probe size, spectroscopic resolution, probe current and primary electron energy can be varied over a large range. This flexibility is particularly important for nanostructures where each of these variables needs to be carefully counterbalanced in order to collect spectroscopic data without altering the integrity of the sample. Here the implementation of valence electron energy-loss spectroscopy to the study of nanostructures is discussed, with particular mention to the theoretical understanding of each of the contributions to the overall spectrum.

PACS: 73.22.−f; 79.20.Uv; 68.37.Lp

Keywords: VEELS; Nanoparticles; Quantum dots

1. Introduction

In traditional advanced electronic systems, the ability of a material to function in a device structure is primarily determined by the fundamental properties of the dislocations, stacking faults and grain/domain boundaries within the active layer, and the interfaces between the active layer and the other components in the device. These extended defects and interfaces invariably act as segregation sites for vacancies and/or impurities, and can be a source of localized electronic states (either from the impurities/vacancies or through dangling bonds caused by the atomic arrangement) [1,2]. Understanding the electronic properties of such systems typically requires characterization of the atomic structure and composition with atomic scale sensitivity; a capability that is, for instance, possible through the combination of Z-contrast imaging and core-loss electron energy-loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM). Numerous examples in the last 10 years have shown that the optimization of a small probe (~0.1 nm) with a high beam current, can enable unique structure–property relationships to be determined in this manner (see, e.g., Refs. [3–6]).

In the case of nanostructured systems, and in particular quantum dots (QD) and nanowires, the presence of extended defects within the active structure is much reduced and it is the properties of the surfaces and their interaction with point defects/impurities that has a large effect on the properties of the system as a whole [7]. A fundamental understanding of the effect that the surface termination/embedding medium has on the overall properties of the QD/nanowire as a function of size, shape and composition is therefore an integral aspect of realizing their potential for a wide variety of applications, such as optics and lasers [8–10], electronics [11], and magnetics/spintronics [12]. Surfaces also play a key role in toxicity/medical applications of QDs [13] and in advanced catalysis [14,15].

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0304-3991/$ - see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.ultramic.2007.07.008

Analyzing these properties in individual nanostructures requires a modified approach to performing imaging and spectroscopy in the STEM. Unlike the extended defects and interfaces that have been studied before, nanostructures have a tendency to move under the intense electron beam, making analysis difficult. In addition, beam damage in the nanostructures can manifest itself as a conformational change, a structural change, or a reaction with the support and/or matrix. The approach of using a small beam with high beam current may therefore not provide the best means to analyze each nanostructure. Furthermore, as the electronic response of the nanostructure as a whole is the most important factor, core-loss spectroscopy does not provide the required spectral information.

Information on the surface and bulk response of materials can in principle be obtained through valence electron energy-loss spectroscopy (VEELS) (see, e.g., Refs. [16]). Depending on the dielectric function for the material in question, the beam energy, and the thickness, there can be multiple contributions to the spectrum—the actual dielectric response of the bulk, surface (interface) plasmons, guided light modes and Cherenkov losses [17]. However, for nanostructures where the thickness in the beam direction is small these effects are either negligible or easily modeled. In addition, by employing an aloof beam [18], beam damage can be reduced and the effect of surface contributions can be identified. By obtaining images and spectra from nanostructures using a combined monochromator and aberration corrector system, the flexibility exists to tailor the beam current and probe size to the nanostructure present. If this is coupled with a variable voltage instrument, then beam damage can also be significantly reduced by lowering the voltage. In this paper, the dielectric theory needed to understand VEELS is discussed for the limiting case of nanostructures of low thickness (<10 nm). In addition, the benefits of a variable voltage monochromated and aberration corrected microscope to obtain the spectra will be highlighted by a short series of experimental results.

2. VEELS of nanoparticles

2.1. Dielectric theory, VEELS and nanostructures

Dielectric theory has successfully been applied to describe the energy losses measured in transmission VEELS. On grounds of the dielectric theory, band-gap and interband transition energies have been measured for various materials (see, e.g., Refs. [19–21]). Bulk dielectric losses as well as losses due to the foil's surfaces have been considered [22]. Furthermore, expressions have been derived that describe energy losses caused by interfaces as well as the loss function of spherical or cylindrical particles, core-shell structures and heterogeneous materials [23–27]. Apart from bulk dielectric losses, that are aimed to be solely measured, and surface effects, VEEL spectra can be affected by retardation effects [17]. Within the dielectric formalism, Kröger [28] derived an expression that describes the energy-loss probability of fast electrons transmitting thin films taking into account bulk dielectric losses as well as surface and retardation effects. Bolton and Chen [29] expanded Kröger's formalism to multilayered systems considering surface, interface and retardation contributions. Hence, for a proper interpretation of VEEL spectra of thin films, relativistic effects and finite sample effects can be important. Some of these issues are resolved, some are unresolved [30].

In principle, the dielectric concept applied to derive expressions for the energy-loss function of thin films of bulk materials can also be applied to nanostructures and individual nanoparticles. On the basis of the dielectric function of the corresponding bulk material, Mie theory [31] opens a way to describe the dielectric response of a small spherical-like particle. Mie theory is the solution of Maxell's equations in spherical coordinates with boundary conditions that describe a spherical particle [31,32]. Equivalent expressions for ellipsoidal particles [33] and shell structures [32,34] have been derived. Recent work by Idrobo et al. [35] showed that in case of clusters of Si atoms, Mie theory is in excellent agreement with the optical response derived from first-principles calculations. This result suggests that for selected (metal-like) materials the dielectric concept of bulk materials can be "extrapolated" to nanosystems consisting of even less than 50 atoms.

However, dielectric theory is a macroscopic theory in a continuum model assuming that the dielectric function does not vary within a given part of the system. Using a dielectric function to describe a nanosystem might not be adequate. Attempting to solve the question "*what is the correct microscopic dielectric function to be used in a nanosystem?*" Cartoixà and Wang [36] find by ab initio calculations that the dielectric response of a quantum dot is not invariant. The dielectric response is bulk-like inside the quantum dot, whereas the reduction of the macroscopic dielectric constant of a quantum dot is caused by a surface effect. Hence, there is no position-invariant dielectric function of QD as this is the case for extended phases. What is measured as the actual, i.e., "overall", dielectric function of a QD is a complex superposition of a varying microscopic dielectric function. However, it is this "overall" dielectric function of a nanostructure that is measured by VEELS in STEM and it is this integral property that defines the functionality of the QD.

Analyzing a bulk material by transmission VEELS, surface effects can interfere with the bulk dielectric response of the material. For nanostructures like QD, thin nanowires or nanotubes, a distinction between surface and bulk contribution is not necessary and not feasible. For common experimental setups, the delocalization of low-loss scattering events limits the spatial resolution [37]. In any case, surface states are an essential part of a nanosystem's electronic structure. Hence, in order to measure the nanostructure's electronic properties it is essentially needed to have the surface contribution