Ultramicroscopy 171 (2016) 166–176

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic

Dark-field image contrast in transmission scanning electron microscopy: Effects of substrate thickness and detector collection angle ☆

Taylor Woehl *, Robert Keller

Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD, United States

ARTICLE INFO

Article history:
Received 12 April 2016
Received in revised form
29 June 2016
Accepted 5 August 2016
Available online 6 August 2016

Keywords:
Transmission scanning electron microscopy
Monte Carlo simulations
Contrast
Image simulations
Scanning transmission electron microscopy
Quantitative microscopy

ABSTRACT

An annular dark field (ADF) detector was placed beneath a specimen in a field emission scanning electron microscope operated at 30 kV to calibrate detector response to incident beam current, and to create transmission images of gold nanoparticles on silicon nitride (SiN) substrates of various thicknesses. Based on the linear response of the ADF detector diodes to beam current, we developed a method that allowed for direct determination of the percentage of that beam current forward scattered to the ADF detector from the sample, i.e. the transmitted electron (TE) yield. Collection angles for the ADF detector region were defined using a masking aperture above the detector and were systematically varied by changing the sample to detector distance. We found the contrast of the nanoparticles, relative to the SiN substrate, decreased monotonically with decreasing inner exclusion angle and increasing substrate thickness. We also performed Monte Carlo electron scattering simulations, which showed quantitative agreement with experimental contrast associated with the nanoparticles. Together, the experiments and Monte Carlo simulations revealed that the decrease in contrast with decreasing inner exclusion angle was due to a rapid increase in the TE yield of the low atomic number substrate. Nanoparticles imaged at low inner exclusion angles (< 150 mrad) and on thick substrates (> 50 nm) showed low image contrast in their centers surrounded by a bright high-contrast halo on their edges. This complex image contrast was predicted by Monte Carlo simulations, which we interpreted in terms of mixing of the nominally bright field (BF) and ADF electron signals. Our systematic investigation of inner exclusion angle and substrate thickness effects on ADF t-SEM imaging provides fundamental understanding of the contrast mechanisms for image formation, which in turn suggest practical limitations and optimal imaging conditions for different substrate thicknesses.

1. Introduction

Characterization of nanomaterial morphology requires robust electron microscopy techniques that yield images with straightforward and easily interpreted contrast. Bright field (BF) or dark field (DF) transmission electron microscopy (TEM) imaging at its most simplistic utilizes amplitude contrast, i.e. the variation in image intensity due to variations in sample mass-thicknesses, to visualize samples at high resolution. However, the premise of BF or DF TEM is to use an objective aperture to exclusion diffracted electrons (BF TEM) or the direct beam (DF TEM), and therefore cannot be used to form atomic resolution images, which are due to interference between unscattered and scattered electrons. Phase contrast TEM is one of the most prolific atomic resolution imaging techniques; however, the coherent nature of image formation makes interpretation of images difficult [1]. To address the problem of the complex contrast formed in atomic resolution phase contrast TEM images, Crewe and co-workers developed annular dark field scanning TEM (STEM), a technique that employed a focused electron probe that was scanned across a sample in a manner similar to scanning electron microscopy (SEM) [2]. In STEM, electrons transmitted through the sample are collected serially by an annular detector to form an annular dark field STEM image (ADF-STEM). This imaging technique was found to be inherently incoherent, with the contrast approximately proportional to the square of the atomic number of the sample, if the scattered electrons were integrated over an annular detector with an inner exclusion angle that was sufficiently large to exclude diffracted electrons. The technique is known as high angle ADF (HAADF) STEM or Z-contrast STEM, and circumvented the long standing problem of contrast reversal in phase contrast TEM imaging [3].

☆Contribution of the U.S. Department of Commerce. Not subject to copyright in the United States.

* Corresponding author.
E-mail address: tjwoehl@umd.edu (T. Woehl).

http://dx.doi.org/10.1016/j.ultramic.2016.08.008
0304-3991/

With recent advances in aberration correction and high tension stability, STEM has achieved a spatial resolution on the order of 50 pm to 100 pm. However, STEM imaging utilizes electron energies ranging from 100 keV to 300 keV, which can induce imaging artifacts such as knock-on damage and low image contrast in low atomic number materials [4]. Practically speaking, the availability of STEM instruments is limited due to the high cost of ownership as well as the expertize needed to perform complex alignment procedures [5]. Often the atomic scale resolution afforded by aberration-corrected STEM is not needed, in which case STEM imaging in a scanning electron microscope (SEM) equipped with a transmission detector (*t*-SEM) is ideal [5–10]. t-SEM retains the advantages of conventional STEM imaging, such as atomic number contrast and incoherent imaging, but is more affordable and does not require the timely STEM alignment procedures. The physics of image formation for t-SEM and STEM are exactly the same; however, the electron optics and practical operation differs between the two techniques, justifying a different acronym for the STEM in the SEM, i.e. t-SEM. Resolutions on the order of 0.5 nm to 1 nm can typically be attained by t-SEM, making it applicable for most imaging experiments that do not require atomic resolution [5]. Additionally, t-SEM has the added advantage of utilizing SEM electron energies (typically 20 keV to 30 keV), which increase the amount of electron scattering and signal from thin samples with low atomic numbers [5]. t-SEM imaging typically utilizes either a retractable solid state STEM detector [11] or a secondary electron converter plate [8]. For the converter plate configuration, transmitted electrons are converted to secondary electrons *via* a polished metal surface that is angled towards the Everhart-Thornley detector with which the t-SEM image is registered [8]. Even though modern t-SEM imaging is still an area of active development, the technique has seen important applications in materials science, chemistry, and life sciences. Several researchers have utilized t-SEM to image carbon-based nanomaterials [6,12], multiphase alloys [6], semiconductor materials [7,11,13,14], polymers [15], nanoparticle uptake into cells [16], and hydrated samples [17,18]. Because t-SEM utilizes relatively low electron energies, Monte Carlo simulations have proven useful for comparison to experiments for determination of sample contrast and resolution [6,13], sample thickness [7,19], and dopant concentration [11].

Due to the increased amount of scattering by the low-energy electrons inherent to t-SEM, imaging artifacts not present in conventional TEM or STEM may arise, such as contrast inversion [6], low signal-to-noise [6,8], and material-dependent contrast mechanisms [15]. The larger Bragg angles associated with low energy electrons, coupled with the relatively small convergence angle of the incident beam, may result in diffraction contrast contributions to ADF t-SEM images for crystalline materials with small lattice spacings (e.g., metals and metal oxides). On the other hand, amorphous polymers, soft materials, and crystalline polymers with large lattice spacings, and consequently smaller Bragg angles, tend to display stronger atomic number contrast (i.e. Z-contrast) for a given collection angle [15]. Nanoparticle size-dependent contrast inversion was observed on thick sample substrates, which restricted the use of image segmentation algorithms for phase identification [6]. Brodusch and co-workers observed a strong dependence of the image contrast on the inner exclusion angle of the ADF detector [6]. While these changes in ADF t-SEM contrast were accurately predicted with Monte Carlo simulations [6], the fundamental mechanism causing them remained unclear. Overall, the structure of the nanomaterial, the thickness and structure of the underlying substrate, and the ADF detector collection angle have been shown to have significant effects on the image contrast and fundamental contrast mechanisms for ADF t-SEM. In order to develop a robust ADF t-SEM technique, the source of these image artifacts and factors controlling contrast mechanisms must be understood at a fundamental level.

The article is organized as follows. We first introduce a method to calibrate the ADF detector, which normalizes images to the incident beam current to facilitate comparison with Monte Carlo simulations. We image gold nanoparticles on silicon nitride substrates of various thicknesses, determine their contrast, and compare the results with Monte Carlo simulations. Contrast artifacts were observed at low ADF inner exclusion angles (< 150 mrad) and on thick substrates (> 100 nm), which we explain with Monte Carlo simulations. Finally, we conclude by suggesting practical limitations and optimal ADF collection angles for imaging nanoparticles on thin and thick substrates with t-SEM.

2. Experimental methods

2.1. Transmission scanning electron microscopy and ADF detector geometry

We performed the imaging experiments in a Leo Gemini 1525 field emission SEM[1] equipped with a retractable solid state transmission detector mounted below the sample (KE Developments, Deben UK). The SEM was operated at 30 kV accelerating voltage. The transmission detector consisted of four 2.75 mm $\times$ 5.4 mm rectangular solid state diodes mounted in a grid within a metal housing (inset Fig. 1a). The rectangular diodes did not have well-defined collection angles, so we used masking apertures to define the active area of the detector (Fig. 1a). The apertures were mechanically attached to the housing and were electrically isolated from the diodes. Note that the masking aperture is not perfectly annular, as the sides are cut off to align with the underlying rectangular diodes (cf. inset Fig. 1a). For further details on the design and use of the modular apertures for t-SEM imaging, please refer to the recent report by Holm and Keller [20]. We estimated the exclusion and collection angles assuming that the aperture was perfectly annular. We define the exclusion angles as the angles below which the direct unscattered electrons are excluded (inner exclusion angle) and above which the highly scattered beam is excluded (outer exclusion angle) from being detected by the transmission detector. The collection angles are defined as the range of scattering angles that are collected on the detector. For all experiments in this article, the inner and outer annulus radii were held constant at $r = 2$ mm and $r_1 = 4$ mm, and the exclusion angles were changed by varying the distance between the sample and masking aperture (d). By varying d from approximately 2–16 mm, the inner exclusion angle was varied between $\beta = 100$–700 mrad (Fig. 1b). The inner and outer exclusion semi-angles are defined by the following relations:

$$\beta = \arctan\left(\frac{r}{d}\right) \tag{1}$$

$$\beta_1 = \arctan\left(\frac{r_1}{d}\right). \tag{2}$$

Here β and β_1 are the inner and outer exclusion angles, r and r_1 are the inner and outer annulus radii, and d is the aperture to sample distance. Because the inner and outer annulus radii were fixed, the collection angles, β_1–β, varied with sample-to-detector distance as well (Fig. 1b). All measurements in this article will be reported as a function of the inner exclusion angle, β.

[1] Commercial tradenames are indicated in this work for technical completeness. Their use does not imply endorsement by NIST, nor does it imply these are necessarily the best products.