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Imaging Si nanoparticles embedded in SiO_2 layers by (S)TEM-EELS

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Abstract

Fabrication of systems in which Si nanoparticles are embedded in a thin silica layer is today mature for non-volatile memory and opto-electronics applications. The control of the different parameters (position, size and density) of the nanoparticles population is a key point to optimize the properties of such systems. A review of dedicated transmission electron microscopy (TEM) methods, which can be used to measure these parameters, is presented with an emphasis on those relying on electron energy-loss spectroscopy (EELS). Defocused bright-field imaging can be used in order to determine topographic information of a whole assembly of nanoparticles, but it is not efficient for looking at individual nanoparticles. High-resolution electron imaging or dark-field imaging can be of help in the case of crystalline particles but they always provide underestimated values of the nanocrystals population. EELS imaging in the low-energy-loss domain around the Si plasmon peak, which gives rise to strong signals, is the only way to visualize all Si nanoparticles within a silica film and to perform reliable size and density measurements. Two complementary types of experiments are investigated and discussed more extensively: direct imaging with a transmission electron microscope equipped with an imaging filter (EFTEM) and indirect imaging from spectrum-imaging data acquired with a scanning transmission electron microscope equipped with a spectrometer (STEM-PEELS). The direct image (EFTEM) and indirect set of spectra (STEM-PEELS) are processed in order to deliver images where the contribution of the silica matrix is minimized. The contrast of the resulting images can be enhanced with adapted numerical filters for further morphometric analysis. The two methods give equivalent results, with an easier access for EFTEM and the possibility of a more detailed study of the EELS signatures in the case of STEM-PEELS. Irradiation damage in such systems is also discussed.
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1. Introduction

The study of materials and devices containing silicon nanocrystals has been extremely active over the past decade, since they display intense light emission and therefore are promising new possibilities in Si-based opto-electronics. Recently, it was also demonstrated that Si nanoparticles (nps) could have applications in micro-electronics, for example, as storage elements within the gate oxide of non-volatile memory devices. These memory devices, consisting of a metal–oxide–semiconductor field-effect transistor (MOSFET) with nps embedded within the gate oxide, are promising candidates for high-storage-density low-power memory applications [1,2]. Multi-dot floating gates consisting of Si or Ge nps have been fabricated by different deposition techniques like thermal oxidation of $Si_{1-x}Ge_x$ or ion implantation followed by annealing [3]. The fabrication of nanocrystals (ncs) memory devices by ultra-low-energy Si ion implantation and subsequent thermal treatment has recently been demonstrated [4]. This fabrication route is very attractive

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because of its ability to control the size and location of the narrow nps band and its compatibility with standard CMOS technology. In practice, high-dose (typically $10^{16}\,cm^{-2}$) Si implantation in the 1 keV range into very thin (up to 10 nm thick) oxide layers followed by annealing (900–1000 °C), allows for the formation of two-dimensional arrays (2D-arrays) of Si nps positioned at direct tunneling distances from the SiO_2/Si interface [5].

The structural characterization of the nps population is crucial for optimizing their electrical properties [6–8]. The relevant parameters are the distance of the nps array to the electrodes, their size distribution, their surface density and the surface fraction (coverage) which they occupy. In particular, the nps density is a key factor as it determines the number of charges stored by the device and/or the number of charges stored per nanocrystal. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) has been applied to detect the presence of Si nps in thin SiO_2 layers [9,10]. But, transmission electron microscopy (TEM) techniques are yet the most powerful ones.

Differentiating between amorphous Si, crystalline Si and SiO_2 by TEM, however, remains a very challenging task. Measuring the distances of the Si nps layer to the electrodes and the width of the layer has already been performed by conventional TEM (defocused bright field) when observed parallel to the plane they form (cross-section) [11]. Imaging individual Si nps in the perpendicular configuration (plan-view) by the same method has not been successful. The nps exhibit only weak amplitude and phase contrast because of the small differences in atomic number and density between Si and SiO_2. Nowadays, size distributions of Si nps in SiO_2 are measured on high resolution electron microscopy (HREM) or dark field (DF) images but only crystalline particles are dealt with. These images are orientation dependent and not all the particles can be visualized. Thus their surface density cannot be measured with confidence.

To overcome this last and very important limitation, we have used imaging techniques relying on electron energy-loss spectroscopy (EELS). With EELS associated to TEM, chemical mapping can be achieved, based on a differentiation method, which does not involve the atomic number or the density but some electronic properties of the chemical phase in which the elements are engaged (i.e. Si and SiO_2). Plasmons are the major signature in the low-energy-loss domain of the EELS spectrum. They correspond to collective oscillations of valence electrons associated with each phase present in the analyzed area, and their energies are mostly governed by their mean electron densities. For bulk silicon and for silica, plasmon energies are 16.7 and 22.5 eV, respectively. They can, therefore, be easily discriminated and used to get images of the relevant phases. Two methods have been implemented to record such characteristic – Si or SiO_2 – images: either, directly forming the image of the area of interest with electrons which have suffered the Si plasmon energy loss, or indirectly forming the image after acquiring individual EELS spectra at each point of the area of interest and extracting from these collection of spectra the distribution in position of the Si plasmon signal. These methods refer to energy-filtered transmission electron microscopy (EFTEM) [12] and spectrum imaging in a scanning transmission electron microscope (STEM-PEELS) [13]. EFTEM has already been employed for the study of Si nps designed for microelectronics and photonics [14]. Since 2003, it has been used to image Si dots prepared by chemical vapor deposition (CVD) and dedicated for photoluminescence [15] and memory applications [16]. STEM-PEELS is applied here for the first time in the case of Si particles embedded within a SiO_2 matrix.

This paper aims to provide a review insight on "imaging Si nanoparticles embedded in a silica matrix" for the community of materials scientists working in this field. We first introduce and discuss the successes and/or limitations of TEM methods. Then, we describe those involving EELS that overcome the difficulties encountered with conventional TEM imaging. A critical analysis of the most employed method, EFTEM, is proposed and some limitations of the use of this technique are pointed out. Two procedures which can be applied to the spectrum images obtained by STEM-PEELS are also discussed and compared. Finally, from these "chemical phase" images and for different cases, from low to high nps density, the size distribution, the nps surface density (number of nps per unit area) and the surface fraction occupied by the nps are measured. A complete study has been performed for two specific families of specimens, involving TEM defocused bright field, TEM DF and HREM in combination with energy filtering. The results of the quantification of the nps densities are compared.

2. Experimental details

Ten-nanometer-thick SiO_2 layers were thermally grown on 8-inch p-type (1 0 0)-oriented Si wafers and subsequently ^{28}Si-implanted with an energy of 1 keV to a dose of 10^{16} and $2\times10^{16}\,cm^{-2}$. Following the implantation step, the samples were furnace annealed for 30 min at different temperatures (950 and 1075 °C) in inert (N_2) or oxidizing (N_2+O_2) ambient. A 60 nm thick poly-Si layer was deposited on top of the oxide to help in visualizing the SiO_2 surface for cross-sectional TEM examination only.

Specimens from all samples were prepared for cross-sectional (XTEM) and plan-view (PVTEM) observations using the standard procedure involving mechanical polishing and Ar^+ ion milling.

HREM and dark-field images were recorded with a CM30 Philips TEM equipped with a standard LaB_6 electron source operating at 300 keV and having a nominal resolution of 0.19 nm.

STEM-PEELS was performed with a field emission scanning TEM, VG-HB 501, operating at 100 kV and equipped with a PEELS spectrometer. A 0.7 nm probe is focused and scanned over the specimen. At each image point (typically 128×128 or 256×256), an EELS spectrum

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