Micron 77 (2015) 57–65

Contents lists available at ScienceDirect

Micron

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

Gentle quantitative measurement of helium density in nanobubbles in silicon by spectrum imaging

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ARTICLE INFO

Article history:
Received 4 March 2015
Received in revised form 19 May 2015
Accepted 19 May 2015
Available online 27 May 2015

Keywords:
EELS
EFTEM
Spectrum imaging
Helium bubbles
Implantation

ABSTRACT

We propose an original method for the determination of the physical properties of nanometer sized helium bubbles using spectrum imaging in an energy-filtered transmission electron microscope. Helium bubbles synthesized by high fluence implantation and thermal annealing in silicon are investigated. The acquisition parameters are determined to optimize both signal/noise ratio and time. The limitations to the extent of observable areas on a typical sample are explained. The necessary data correction and helium K-edge position measurement procedures are detailed and the accuracy of the method is discussed. Finally helium density maps are obtained and discussed.

1. Introduction

When introduced in high concentration in materials, helium tends to agglomerate and form nanometer-sized bubbles (Donnelly and Evans, 1991; Raineri and Saggio, 2000; Cerofolini et al., 2000). For instance, helium bubbles can be synthesized using ion implantation. Specific implantation and annealing parameters in a given material lead to reproducible results, which allow the study of those bubbles and their contents in a statistical way. Helium bubbles can also be obtained as a by-product of nuclear reactions, as charged α particles are emitted and eventually impact either the walls, or the fuel inside a nuclear reactor (Guilbert et al., 2003). Helium bubbles usually have detrimental effects on the materials in which they are embedded; in the nuclear-energy context, embrittlement is an important one (Trinkaus and Singh, 2003). But in the microelectronic field they can have several applications such as impurity gettering (Petersen et al., 1997) and production of silicon on insulator (SOI) wafers using the layer splitting by ion cutting process (Bruel, 1995; Agarwal et al., 1998). Moreover, low energy helium plasma treatments have recently received considerable interest for nanostructuration of surfaces with applications in domains of energy conversion and storage devices, by both bottom-up (Godinho et al., 2013) or top-down approaches (Kajita et al., 2013; Iyyakkunnel et al., 2014). In particular, nanopores in amorphous silicon coatings produced using such methods have been revealed to contain a high helium density (Schierholz et al., 2015). In any case, in order to better predict these effects and their properties, and to control them, extensive study of bubble formation and evolution mechanisms under annealing or irradiation is a prerequisite.

The important parameters required to validate growth models are the size, morphology, and helium density of the bubbles. The helium density can then be converted to pressure in the bubbles through an appropriate equation of state (Trinkaus, 1983; David et al., 2014). Conventional transmission electron microscopy (TEM) can be used to obtain the size and morphology of the bubbles, but the determination of their helium density requires a more complex approach. One such approach is the measurement of diffraction contrast features in TEM micrographs (Tillmann et al., 2004). However it is not well adapted to the study of spherical nano-bubbles. Indeed, the strain field in that case leads to more complex contrasts in dark field or bright field imaging than that which is observed for platelet defects, and these contrasts are tricky to be used for quantification. Another powerful approach is spatially-resolved electron energy-loss spectroscopy (EELS) using scanning TEM (STEM). This method has been used for bubbles embedded in various matrices (Schierholz et al., 2015; David et al., 2014, 2011; Manzke et al., 1982; Jaeger et al., 1982, 1983; McGibbon, 1991; Walsh et al.,

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http://dx.doi.org/10.1016/j.micron.2015.05.011
0968-4328/

2000; Taverna et al., 2008; Frechard et al., 2009). However, we have demonstrated that it can show an adverse effect when helium bubbles are embedded in silicon or germanium (David et al., 2014, 2011), as it can trigger helium detrapping upon electron irradiation from the probe. This has recently been observed in the case of helium nanopores in silicon as well (Schierholz et al., 2015). While this process is slow enough for a one-time measurement, it effectively renders repetition of the same measurement unfeasible. This hinders the application of STEM-EELS in a conventional TEM/STEM for He density measurements during *in situ* experiments, as those require several scans on each analyzed bubble upon, for instance, annealing or irradiation.

A possible alternative to STEM-EELS is spectrum imaging in an energy-filtered TEM (EFTEM-SI), which is based on the acquisition of a series of energy-filtered images at different energy-losses (Jeanguillaume and Colliex, 1989; Lavergne et al., 1992; Verbeeck et al., 2004).

EFTEM-SI has been shown to be a powerful tool to gather information in the low loss part of the spectrum, for example for plasmon imaging (Eggeman et al., 2007; Schaffer et al., 2009, 2010; Nelayah et al., 2009; Sigle et al., 2010) for instance. Moreover, with the EFTEM approach, the illumination conditions are drastically different from STEM-EELS, in terms of current density in particular, as a parallel beam is used instead of a focused probe. This may reduce some effects of electron beam damage, as was recently observed in $LiFePO_4$ (Sugar et al., 2014) and also in polymers (Allen et al., 2011). Our hypothesis was that helium detrapping under the electron beam would be negligible with an EFTEM-SI approach. EFTEM-SI is further useful for the acquisition of maps over large fields of view using relatively short acquisition times, and is hence more suitable than STEM-EELS based approaches when observing a large amount of bubbles. It is thus a potentially valuable technique to investigate the physical properties of helium bubbles in a statistical way.

Here, we describe and validate a method using EFTEM-SI for the determination of the helium density in nano-bubbles in silicon.

2. Sample preparation

The samples used for this study were implanted with 50 keV helium ions at a fluence of $7.5{\cdot}10^{16}$ at.cm^{-2}. The implantations were performed on mono-crystalline p-type Si wafers. The samples were then annealed at temperatures of 500 or 700 °C, chosen for their known results in terms of microstructure, and expected different characteristics of the helium bubbles (size, morphology, He density, pressure) (David et al., 2011).

After implantation and annealing, the Si wafers were mechanically cleaved, wire-sawed and glued face-to-face, in order to obtain cross-sections of the implanted material. The samples were then thinned by diamond disk polishing down to 10 μm in thickness. Finally, they were made electron-transparent *via* PIPS ion polishing down to 60 nm in thickness or less. The parameters for this step, 2.5 keV ion energy and ±8° angle, were chosen to avoid sample damage.

The microstructure of the studied samples is shown in Fig. 1. The chosen implantation and annealing conditions lead in both cases to a dense system of bubbles. The bubbles are situated in a wide band, located between 200 and 400 nm from the sample surface. They can be classified in two groups: small bubbles making up the major part of the band, and large bubbles forming a line at its deepest edge. The different annealing temperatures yield different sizes and densities of bubbles, with greater diameters and fewer bubbles for the 700 °C samples than for the 500 °C samples. More specifically, after the 500 °C annealing, small bubbles are typically below 5 nm in diameter, while the larger ones exhibit a mean diameter of 10 nm. In 700 °C annealed samples, the bubble diameter is higher, typically up to 10 nm for the smallest ones, while the largest ones can reach 20 nm in diameter. In this study we will mainly focus on bubbles exhibiting a diameter of 10 nm or more.

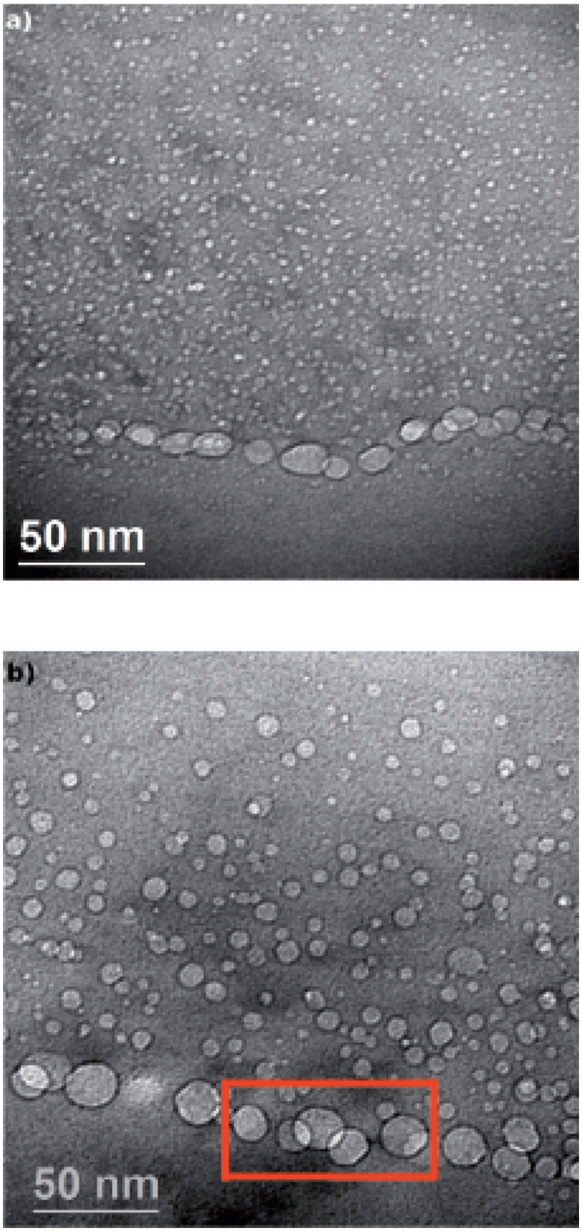

Fig. 1. Zero loss EFTEM images of Si samples implanted with 50 keV, 7.5 × 10^{16} cm^{-2} helium ions and annealed at (a) 500 °C and (b) 700 °C, filtered over the elastic peak with a 1 eV slit.

3. EFTEM helium density determination

3.1. Data acquisition

The microscope used for this study is a JEOL 2200FS with FEG operated at 200 keV, equipped with an in-column Ω filter and a Gatan Ultrascan 2048 × 2048 pixel CCD camera. Prior to data acquisition, the sample is oriented to minimize diffraction contrast in the observed area and an objective aperture is inserted giving a collection semi-angle for the spectrometer of 5.65 mrad. A nominal 100k× magnification, resulting in a final 200 nm × 200 nm field of view on the CCD, was chosen here in order to observe ten or more of the large bubbles simultaneously. Since helium densities are to