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A Straightforward Method for Measuring the Elastic and Inelastic Mean Free Paths for Scattering of Fast Electrons in Technologically Important Thin-Film Oxides

Adham Basha[1], George Levi[1], Tamir Amrani[1], Yang Li[2], Guy Ankonina[2], Pini Shekhter[3], Lior Kornblum[2], Ilan Goldfarb[1] and Amit Kohn[1*]

[1.] Department of Materials Science and Engineering, The Iby and Aladar Fleischman Faculty of Engineering, Tel Aviv University, Ramat Aviv, Tel Aviv, Israel.
[2.] Andrew and Erna Viterbi Faculty of Electrical and Computer Engineering, Technion – Israel Institute of Technology, Haifa, Israel.
[3.] Tel Aviv University Center for Nanoscience and Nanotechnology, Tel Aviv University, Ramat Aviv, Tel Aviv, Israel.
* Corresponding author: akohn@tauex.tau.ac.il

Thin-film oxides are a primary building block in many devices and have a wide range of applications, such as optoelectronics, spin-electronics, energy harvesting and storage, memristive devices, and optical coatings [1–7].

Transmission Electron Microscopy (TEM) is widely implemented for quantitative structural characterization of nano-scale volumes oxides due to its high scattering cross-section and small probe size [8, 9]. Quantitative TEM often requires accurate knowledge of sample thickness for determining properties such as: defect density, structure factors, sample dimensions and geometry. Furthermore, an accurate measurement of sample thickness is necessary for the modelling image formation, estimation of electron beam or X-ray signal broadening, and radiation damage evaluation.[10–14].

Reported methods for direct measurement of the TEM sample thickness by a trigonometric-tilt series [15] and contamination-spot separation [16] suffer from complexity and poor accuracy. Convergent beam electron diffraction offers improved accuracy [17, 18], but is a very localized measurement, limited to crystalline materials, and susceptible to beam damage [19].

Conversely, indirect thickness measurement using Electron Energy Loss Spectroscopy (EELS) or Energy-Filtered (EF) TEM can be applied effectively on both crystalline and amorphous materials [10–12, 14, 20–22]. The drawback is that sample thickness is measured in units of inelastic Mean Free Path (MFP). The MFP value can be determined by calibrating EELS measurements using a perpendicular cross-section[12, 20] or conical needle samples[10, 23] prepared by Focused Ion Beam (FIB). However, these methods are limited since the MFP is measured per material and is dependent on several parameters, for example: Energy of the incident electron beam, and collection angle into the spectrometer. Consequently, to date, MFP values are not reported for many technologically important thin-film oxides. Furthermore, measuring the Elastic MFP is also essential for calculating the optimal sample thickness required for quantitative structural characterizations of amorphous materials (e.g., short-range order) [24]. **Hence, a versatile and reliable method is required to enable the extraction of inelastic and elastic MFP values of fast electrons, specifically for thin-film oxides.**

We propose a straightforward calibration methodology for determining the inelastic and elastic MFP of fast electrons in technologically important thin film oxides deposited on high-quality single-crystal semiconductors, typically silicon. Our method is based on accurate measurement of the IMFP of

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electrons in crystalline silicon using indirect EFTEM thickness mapping of Si samples with a range of thicknesses.

These thicknesses are calibrated by a second perpendicular cross-sectioning of TEM samples of several thicknesses using FIB. The IMFP is then determined at nanometer scale accuracy for 80keV and 200keV electrons and a range of collection angles. Following this, the MFP of oxides is determined by measuring the thickness ratio at their interfaces with Si. We demonstrated this method for technologically important thin-films oxides: Ta_2O_5, HfO_2, TiO_2, Al_2O_3, ZnO, SiO_2 (variants: thermal/CVD) and low-κ SiOCH.

The precision of this method was improved by implementing a TEM sample wedge preparation technique, which provides large sampling areas with uniform thickness. [25] Samples were mechanically polished to a thickness of 1-5 μm at the region of interest at a wedge angle of ~1-2˚. Mechanical polishing is followed by a short period of Ar ion milling. These TEM samples enable meaningful statistical averaging of thicknesses adjacent to the Si/Oxide interface and reduce errors due to local thickness variations.

Oxide thin-films were deposited on Si/SiO_2 substrates using either atomic layer deposition, chemical vapor deposition or magnetron sputtering. Their composition, chemical bonding and density were verified by X-Ray Photoelectron Spectroscopy and X-Ray Reflectivity.

The thickness of the TEM samples in units of electron mean free path, inelastic or elastic, was determined from Energy-Filtered (EF) TEM images using intrinsic electron scattering lengths based on Poisson statistics, resulting in a log-ratio equations, (Eq. 1a) for inelastic scattering and (Eq.1b) for elastic scattering [14]:

$$\frac{t}{\lambda_{inelastic}} = \ln(\frac{I_t}{I_0}) \tag{1a}$$

where t is the sample thickness, $\lambda_{inelastic}$ is the inelastic scattering MFP, I_0 is the intensity of the zero-loss image (intensity of electrons transmitted without energy-loss), and I_t is the total intensity without energy filtering, which is equivalent to the intensity of an entire EEL spectrum for a given collection semi-angle, β.

For the elastic scattering MFP, $\lambda_{elastic}$:

$$\frac{t}{\lambda_{elastic}} = \ln(\frac{I_0}{I_u}) \tag{1b}$$

where I_u is the image intensity of the un-scattered electrons, achieved by inserting the smallest objective aperture available (10μm in diameter), equivalent to 2mrad angular spread, to the zero-loss images. The combination of the 10eV energy slit and 2mrad objective aperture excludes the majority of both inelastically and elastically scattered electrons [26].

Calibrated IMFP values of 200keV and 80keV electrons in crystalline Si(001) as a function of collection semi-angle are shown in Fig. (1). For example, the IMFP was measured at 145 ± 4 nm for 200keV electrons and a large collection semi-angle (β=157mrad), in agreement with previously reported values [27, 28].

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The thickness of the oxide films was determined at the Si/Oxide interface using the well-calibrated Si IMFP values measured by FIB perpendicular cross-sectioning. The validity of our proposed ratios method at Si/Oxide interfaces was verified by FIB cross to cross sectioning of the TEM samples. For example, the Secondary Electrons Scanning Electron Microscope (SE-SEM) image shown in Fig. (1) demonstrates uniform sample thickness adjacent to interfaces. Examples of IMFP and EMFP values as a function of electron energy are shown in Fig. (2) for SiO_2 and Ta_2O_5. Similarly, measured and calculated MFPs are summarized for thin-film oxides: HfO_2, TiO_2, Al_2O_3 and ZnO. (Fig. (2c)). For comparison, MFP values were calculated using the Wenzel and Iakoubovskii models for elastic and inelastic scattering, respectively [27, 29].**This work demonstrates a fast and reliable method for the extraction of MFP values in oxides thin films grown on Si substrates. The method relies on accurate measurement of inelastic MFP values of electrons in crystalline Si using EFTEM thickness mapping and FIB perpendicular cross-sectioning. Using this method, elastic and inelastic MFPs for technologically important oxides were measured: Ta_2O_5, HfO_2, TiO_2, Al_2O_3, ZnO, SiO_2 (variants: thermal/CVD) and low-κ SiOCH [30].**

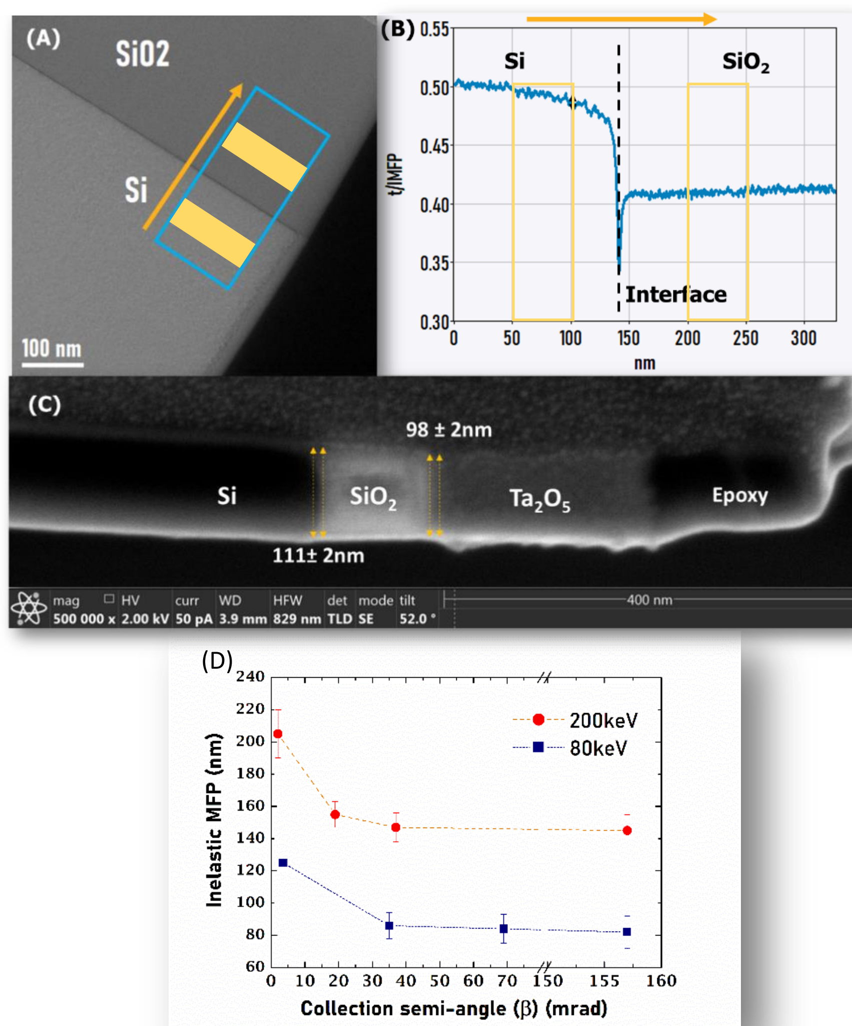

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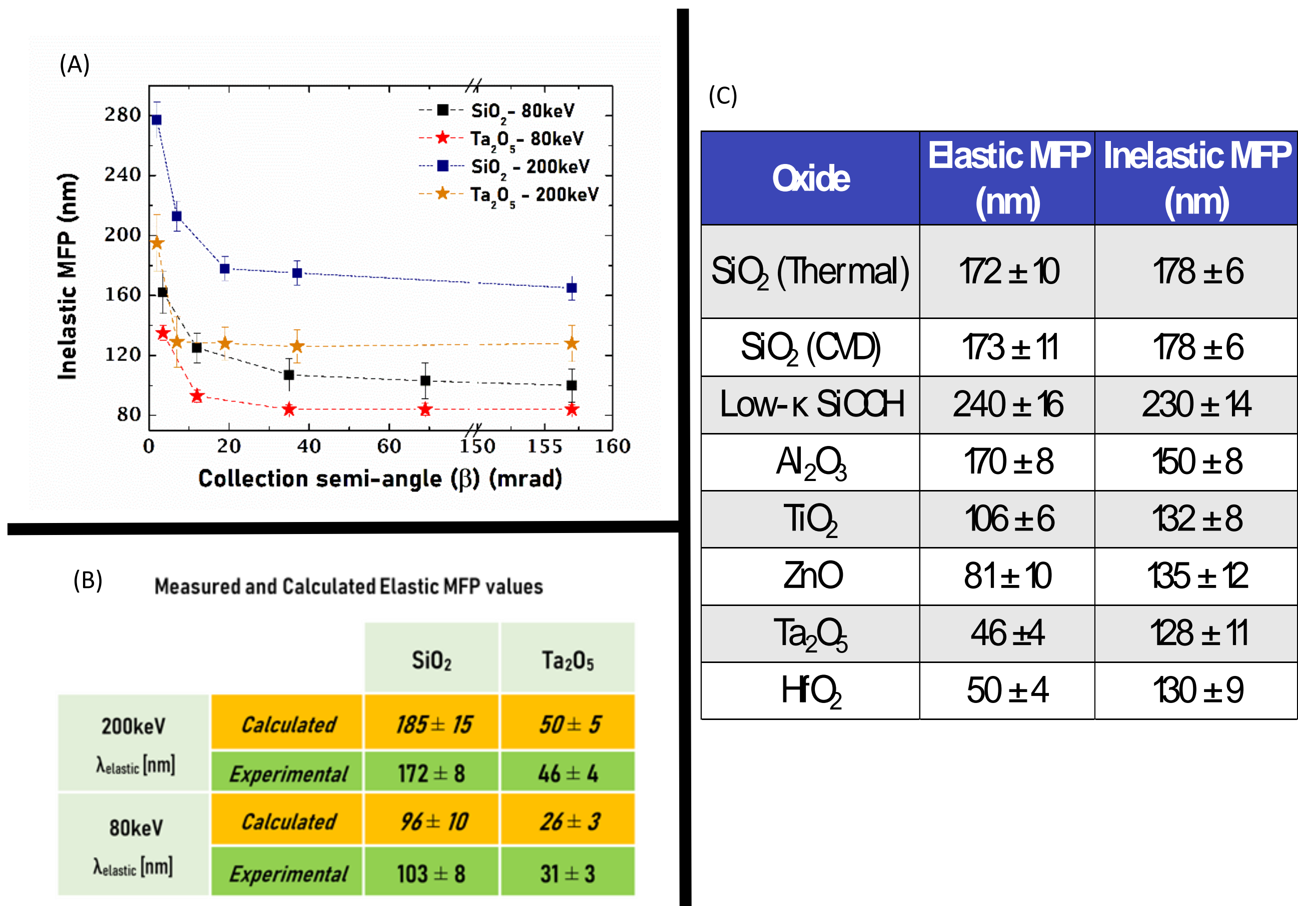
Figure 1.

(A) Energy-filtered TEM thickness map obtained from a SiO_2/Si FIB cross-sectional sample. The thickness profile in units of IMFP is acquired from the area denoted by the blue rectangle.

(B) Average thickness profile in IMFP units adjacent to the Si/SiO_2 interface from which the MFP ratio is extracted. The thickness in IMFP units is acquired from averaging the areas denoted by the orange rectangles.

(C) SE SEM image of a cross-to-cross FIB section from a similar sample. The sample thickness is uniform adjacent to interfaces, thus verifying extraction of MFP values by our proposed ratios approach.

(D) Measured IMFP of 200keV and 80keV electrons in crystalline Si vs spectrometer collection semi-angle, β. These values serve as calibrations for determining MFP values in different oxides grown on Si substrates.



(B) Measured and Calculated Elastic MFP values

		SiO_2	Ta_2O_5
200keV $\lambda_{elastic}$ [nm]	*Calculated*	*185 ± 15*	*50 ± 5*
	Experimental	172 ± 8	46 ± 4
80keV $\lambda_{elastic}$ [nm]	*Calculated*	*96 ± 10*	*26 ± 3*
	Experimental	103 ± 8	31 ± 3

(C)

Oxide	Elastic MFP (nm)	Inelastic MFP (nm)
SiO_2 (Thermal)	172 ± 10	178 ± 6
SiO_2 (CVD)	173 ± 11	178 ± 6
Low-κ SiCOH	240 ± 16	230 ± 14
Al_2O_3	170 ± 8	150 ± 8
TiO_2	106 ± 6	132 ± 8
ZnO	81 ± 10	135 ± 12
Ta_2O_5	46 ± 4	128 ± 11
HfO_2	50 ± 4	130 ± 9

Figure 2.

(A) Measured Inelastic MFP of 200keV and 80keV electrons in SiO_2 and Ta_2O_5 as a function of the collection semi-angle (β).

(B) Measured and calculated Elastic MFP of 200keV and 80keV electrons in SiO_2 and Ta_2O_5 in comparison to calculated values. MFP values were calculated using the Wenzel model for elastic scattering [27].

(C) Measured Inelastic (β~19mrad) and Elastic MFP of 200keV electrons in various oxide thin films.

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