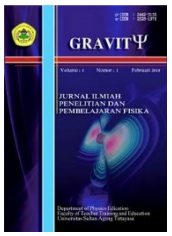
Gravity: Jurnal Ilmiah Penelitian dan Pembelajaran Fisika

http://jurnal.untirta.ac.id/index.php/Gravity

ISSN: 244-515x; e-ISSN: 2528-1976

Vol. 7, No. 2, August 2021, Page 78—84



Monte Carlo simulation on TiO_2: water thickness determination and electron scattering study on wet material

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(Received: 15 June 2021; Accepted: 14 August 2021; Published: 30 August 2021)

ABSTRACT

Analysis of the three-dimensional (3D) structure of a material is indispensable in various fields of science, especially in materials science. Several studies have been conducted to observe the 3D structure of wet samples in a water-soluble environment using ESEM (Environmental Scanning Electron Microscopy) with tomography. The principle of tomography is based on the acquisition of a series of image projections at different angles of inclination and the calculation of the volume of the 3D reconstruction with a special algorithm. In this study, Monte Carlo simulation was used to analyze the optimum water thickness that could be detected in TiO_2 wet material and the number of electron scattering captured to calculate the interaction volume dimensions. The results showed that the optimum thickness was achieved at 400 nm for the thickness of the wet sample and 10 nm for the thickness of the water.

Keywords: electron, monte carlo, thickness, TiO_2

DOI: 10.30870/gravity.v7i2.11592

INTRODUCTION

Several types of materials contain or are dispersed in water during the process, both organic and inorganic materials (Xiao et al., 2018). For example, biological cells contain a high fraction of water. Latex suspensions, consisting of polymer particles dispersed in water, are used for various applications, including for paints, glues or as a binder for superinsulators (Foray et al., 2012). In inorganic materials there are materials which in the process must be dispersed in a liquid, for example in some ceramics, to obtain ceramics with high density, a dispersion process using liquid and surfactants is required (Yu et al., 2008) (Spina et al., 2012)

Ceramics involve nanoparticles that are synthesized directly in a liquid, through a chemical or physical process. In all cases, a complete understanding of the dispersion in suspension is useful for understanding the properties of the material. At the nanoscale and mesoscales, electron microscopy is a key technique (Stahlberg & Walz, 2008). Environmental scanning electron microscopy (ESEM) can also be used to study liquid suspensions. With differential pumping, the pressure in the sample chamber can reach

several tens of Torr. The use of the Peltier stage in ESEM makes it possible to observe objects in a fully hydrated state (Donald, 2003) (Stokes et al., 1998). Condensation and evaporation of water can be carried out on the spot by changing the pressure in the sample chamber. Wet material has been successfully observed in ESEM using secondary electron or backscattering electron detectors (Stokes et al., 1998), a collection of detectors placed under a liquid droplet has proven to be an efficient mode of observation (Bogner et al., 2005).

Tomography is a key characterization tool in materials science and biology. The principle of tomography is based on obtaining a series of projected images at different angles of inclination, and on calculating the volume of a three-dimensional (3D) reconstruction (tomogram) using a special algorithm (Masenelli-Varlot et al., 2014). Bogner et al (Bogner et al., 2005) have described the utility of the combined STEM-in-SEM and ESEM, and this idea was behind the development of the wet STEM imaging mode. Reimer et al have characterized certain samples in various transmission modes and have highlighted beam widening through sample thickness. They have shown that resolution, which is directly related to probe size, is subject to a top-down effect. The use of thin samples thus results in better resolution, avoiding the probe extending through the thickness of the sample.

In previous studies, an analysis of the determination of the minimum water layer in the MCM-41 sample was carried out using wet -STEM (R. F. Septiyanto et al., 2014). The Scanning Transmission Electron Microscopy (STEM) configuration of Environmental Scanning Electron Microscopy (ESEM) provides a new approach for characterizing the 3D structure of materials and optimizes the compromise between resolution levels of several tens of nm and large tomogram sizes due to the high transparency thickness. In addition, STEM enables the transmission of 2D observations of wet samples in ESEM by controlling the sample temperature and the water pressure of the sample environment (R. F. Septiyanto et al., 2014). We used Titanium dioxide for the material sample.

Titanium dioxide, also called titania, has the family of transition metal oxide. Titania is the naturally occurring oxide of titanium, chemical formula TiO_2 (Haider et al., 2019).

In this study, we perform a measurement study via simulation of electron-matter interactions for electron tomography in ESEM, which enables the acquisition of image sequences on wet samples. The example used is alumina material which is widely used in ceramic engineering in industry. Then, a Monte Carlo simulation will be used to estimate the optimum amount of water that can be detected in the wet sample.

RESEARCH METHODS

This research method is a simulation using Hurricane software, which can be installed on a computer or laptop with a minimum specification of Windows XP or Windows 7.

In this simulation, it is necessary to pay attention to the important parameters of the STEM tomography technique.

The tomo-STEM electron tomography technique consists of three main parts, namely: (a) tilting system, (b) system for keeping the target area in the field of view, (c) detection system (Jornsanoh et al., 2011). The functions of these parts are as follows: (a) the tilting system is a large microscope chamber enabling the introduction of a piezoelectric system for rotation of more than 360° around the horizontal axis; rotation is done accurately. (b) System for keeping the area of interest in the field of view: a translational piezoelectric system is used to place the desired area in the eucentric position prior to acquisition of the image series. Then, the positioning that good of the area of interest during the acquisition is ascertained by the movement of the ordinary microscope stage. (c) Detection system: for wet STEM imaging conditions, the annular detector is dedicated to backscattering. The collection of electrons is removed from its position and placed under a thin sample, the electrons are scattered (transmitted indirectly) through the sample. The entire device is controlled and customized via the LabView software interface.

The three-dimensional structure was then reconstructed using traditional software including TomoJ (Jornsanoh et al., 2011).

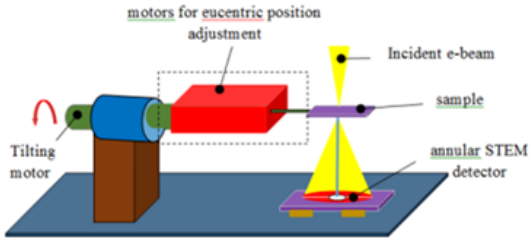

Figure 1. Electron tomography

In this study, we used the electron scattering collection method using Hurricane software from SAMx with Monte Carlo simulation. This research has also previously been carried out using a Monte Carlo simulation with Hurricane software with MCM-41 (R. F. Septiyanto et al., 2014) (Masenelli-Varlot et al., 2014), Prior to the simulation, the first step is to determine the sample, which can be a pure compound or a mixture. The compound used is titania TiO_2, with a layer of water and without a layer of water which will be seen through the simulation. We entered the alumina compound by selecting the compound menu provided in the Hurricane software, which contains some information regarding the compound to be used in the simulation. We used an accelerating voltage of 30 keV for the simulation as defined for the experiment. The simulation parameters include the ability to specify the number maximum trajectory achieved during the simulation. We selected 100,000 passes for simulation and usually the higher the number of passes the slower the simulation process. The sample structure used in the simulation meets the following criteria: x = 5000 nm, y = 5000 nm, and for the z-axis, thickness variations from 200 nm to 4000 nm are used.

The batch simulation mode has been specially designed to allow multiple simulations to be carried out sequentially and simultaneously, with or without variations in deposit thickness. This is especially useful when simulations must be performed while changing one of the simulation parameters. For the simulation in this work, a spherical liquid precipitate with a radius of 1000 nm and thickness with variations of the liquid layer at 10 nm, 20 nm, 30 nm, 50 nm, 100 nm was used. To determine the optimum water film thickness, we set the contrast variation to 5%. The following are the stages of the flowchart in this study as follows.

For all materials, we have sample structure with the computation box: x = 5000 nm, y = 5000 nm, and for z axis, we have variable thicknesses from 200 nm to 4000 nm. The liquid water precipitate is of a spherical shape with a radius of 1000 nm and with the variable thicknesses of 10 nm, 20 nm, 30 nm, and 100 nm. We used scattering collected electron of method this simulation and presented by trajectories of electrons in result of Hurricane software simulation. Interaction of the incident electrons with the target sample will be treated statistically.

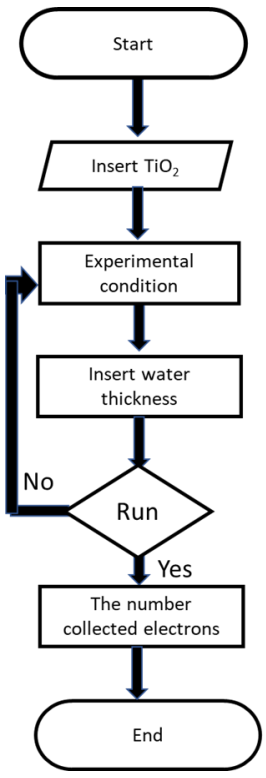

Figure 2. Stage of Monte Carlo simulation with the variation TiO_2 and water thickness

RESULT AND DISCUSSION

The results of the Monte Carlo simulation

using Hurricane software, the calculation of the number of electrons collected for variations in TiO_2 thickness is shown in Figure 3. This curve shows variations in thickness and without overlapping air. Meanwhile, the number of scattered electrons collected is increasing, until the thickness is less than 1000 nm. After that, the number of scattered electrons decreased further to a thickness of 4000 nm. After that thickness, no more electrons are scattered.

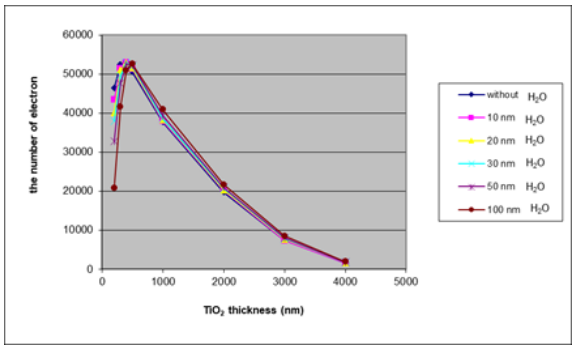

Figure 3. The results of the Monte Carlo simulation on the variation of TiO_2 thickness with the number of scattered electrons electron

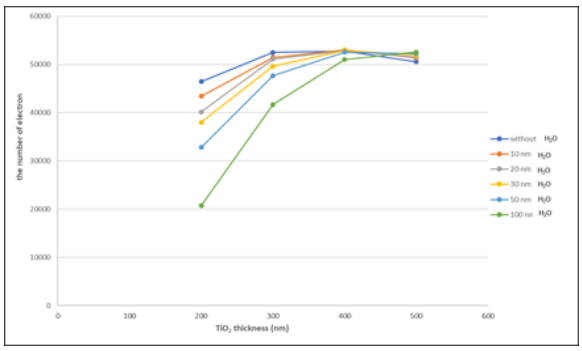

Figure 4. Magnification of the curve for figure 3: Monte Carlo simulation results

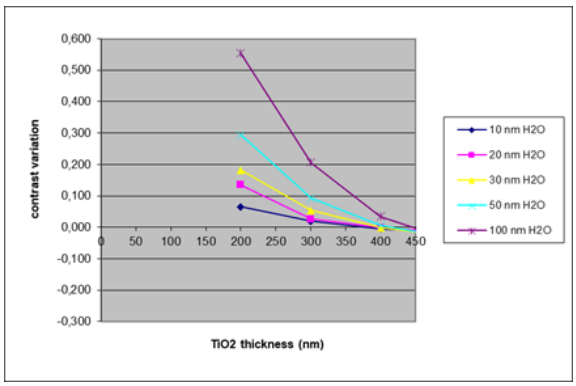

Figure 5. Contrast variation in thickness water and thickness variation

If we enlarge the image, the highest number of scattered electrons will be seen more clearly. In this condition, it was achieved at 10 nm water thickness with TiO_2 sample at 400 nm thickness. There is an effect of the number of electrons adding water to the TiO_2 sample. From the graph shown in Figure 4, it can be seen that the highest number of scattered electrons is found in the 400 nm thickness of the TiO_2 sample, both without water thickness and with water thickness. However, the highest number of scattered electrons occurred at 500 nm TiO_2 thickness and 100 nm water thickness. Above 500 nm thickness, the number of scattered electrons in the TiO_2 sample decreased both with and without water thickness.

When the partial pressure of water is increased, water condenses on the sample, which results in variations in contrast. The expected change in contrast between dry and wet conditions is shown in Figure 5. This provides information about the possibility of detecting a water film on TiO_2. In order to determine the optimal thickness of the water, we have set the contrast variation to be greater than 5%(R. F. Septiyanto et al., 2014) (Masenelli-Varlot et al., 2014) (F. Septiyanto, 2021).

Determination of the optimum water layer that can be detected by taking the thickness of TiO_2 with a contrast variation of more than or equal to 5% the results are shown in Figure 4. The optimal contrast variation has been selected at 5%. Dry to wet conditions are indicated by the increasing thickness of TiO_2. Contrast variation of 5% is indicated for each TiO_2 thickness. The optimum water thickness obtained from the contrast variation has been determined for each sample thickness.

Contrast variation is calculated from the Monte Carlo simulation to explain how a particular region can be distinguished from the water layer. The formula used is shown below:

$$Contrast\ variation = \frac{N_{dry} - N_{wet}}{N_{dry}} X\ 100\% \quad (1)$$

Where Ndry and Nwet correspond to the number of electrons collected in the desired region with no water layer and in a pure water

layer of the same thickness. (Xiao et al., 2018).

In particular thickness of a material, the thicker the material the greater the optimum thickness of water is found, it means that in these circumstances the amount of electron scattering that caught the bigger so contrast images obtained more clearly.

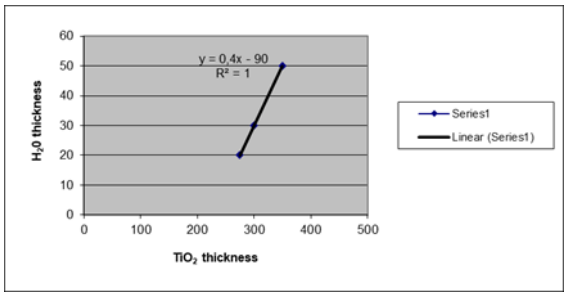

Figure 6. Contrast variation in TiO_2 when electrons are collected in optimum water layer

The optimum water layer thickness that can be detected is 20 nm, 30 nm, and 50 nm on TiO_2 with a thickness of 275 nm, 300 nm, and 350 nm, respectively. Interestingly, the relationship between optimum water thickness and TiO_2 sample thickness is linear (as shown in Figure 6). In Figure 6, three of the five water resistance data are taken, the three data taken are data that show perfect linearity. Figure 6 also shows the relationship between the optimum value of water and the thickness of TiO_2, indicating that the greater the thickness of TiO_2, the greater the optimum value of water required. This shows that the greater the thickness of TiO_2 and water, the greater the number of electrons captured by water in the annular dark field. This is closely related to previous research on other materials (MCM-41) (R. F. Septiyanto et al., 2014) and on Al_2O_3 (F. Septiyanto, 2021) shows the linearity. However, the optimal thickness of water is only available up to a thickness of 0.4 micrometer TiO_2 and 10 nm of water. If the thickness of TiO_2 and water is added continuously, more and more electrons are reflected from the circular dark field. This the contrast of the image obtained is increasingly unclear.

From the Kanaya-Okayama formula shown in equation (2), we can determine the dimensions of the interaction volume of a simple material, namely Carbon. In parallel the Monte Carlo simulation of the "bulk material" provides electron trajectories, the limiting of which is the interaction volume (as shown in Figure 7 for the TiO_2 example). We have several material thickness parameters with a computational box sample structure: x = 33,000 nm, y = 33,000 nm, and z = 20,000 nm. This parameter is used to get the dimensions of the interaction volume.

On carbon, the interaction volume dimension from the Monte Carlo simulation was found to be equal to 8 microns, which is in agreement with what can be obtained by the Kanaya-Okayama formula (9 microns). This validates the way we draw the interaction volume boundaries from the Monte Carlo results, and it also makes it possible to define the interaction volume dimensions for all the studied material. Obviously, the size of the interaction volume is a strong function of the energy of the incident beam as well as the structure and density of the chemical. Here's the formula for Kanaya Okayama:

$$R = \frac{0.0276AE^{1.67}}{Z^{0.89}} \qquad (2)$$

Where R is dimension of interaction volume, A is atomic weight (g/mol), Z is atomic number, r is density $(g/cm)^2$, and E is beam energy (keV).

It is noteworthy that the Kanaya-Okayama formula can be used for single atomic materials only. The dimensions of the interaction volume can also be determined with the trajectories of Monte Carlo simulation. It could be interesting to compare the result of the calculation of Kanaya-Okayama Formula and the one from the trajectories of Monte Carlo simulation.

Figure 7 shows the electron trajectories used to calculate the dimensions of the interaction volume or the depth that the electrons can reach as shown in the Monte Carlo simulation. When the incident ray is fired, the electrons will be scattered marked by electron traces, this Monte Carlo simulation explains the existence of traces of electrons fired by the incident beam with an energy of 30 kV.

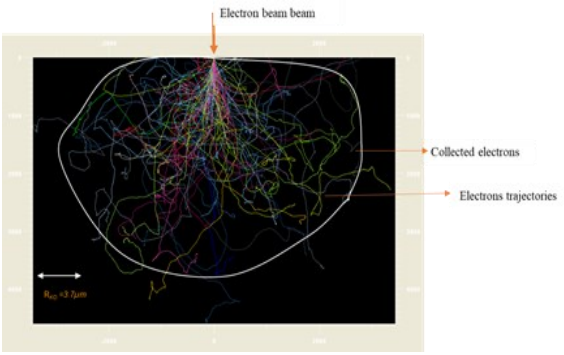

Figure 7. Shows the trajectory of electrons used to calculate the dimension of interaction volume or depth that can be reached by electrons as shown in Monte Carlo simulations with TiO_2 sample

CONCLUSION

Image contrast simulations in STEM-in-SEM simulating the experimental configuration have been investigated. Special software based on the Monte Carlo method (Hurricane software) has been used to calculate the paths of 100,000 electrons. With the Monte Carlo simulation, we have been able to calculate the optimum thickness of the water layer that can be detected in several materials. The relationship between optimum water film thickness and sample thickness is considered to be linear, but the equation depends on the chemical structure of the sample and its density.

The empirical relationship between the optimum water layer thickness and the sample layer, which also involves a measure of the interaction volume and sample density. In future work, it will be interesting to test the validity of the empirical equations we determined, for example by analyzing the behavior of new materials.

ACKNOWLEDGMENT

The author would like to thank all related parties who helped the process of this research, especially to Prof. Karine Masenelli Varlot - MATEIST INSA Lyon France, and Dr.Eng. Ferry Iskandar, M. Eng - ITB Bandung.

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