



# An analysis of the impact of native oxide, surface contamination and material density on total electron yield in the absence of surface charging effects



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## ABSTRACT

The effects of the presence of a native oxide film or surface contamination as well as variations in material density on the total electron yield (TEY) of Ru and B<sub>4</sub>C were assessed in the absence of any surface charging effect. The experimental results were analyzed using semi-empirical Monte Carlo simulations and demonstrated that a native oxide film increased the TEY, and that this effect varied with film thickness. These phenomena were explained based on the effect of the backscattered electrons (BSEs) at the interface between Ru and RuO<sub>2</sub>, as well as the lower potential barrier of RuO<sub>2</sub>. Deviations in the material density from the theoretical values were attributed to the film deposition procedure based on fitting simulated TEY curves to experimental results. In the case of B<sub>4</sub>C, the TEY was enhanced by the presence of a 0.8-nm-thick surface contamination film consisting of oxygenated hydrocarbons. The effect of the low potential barrier of the contamination film was found to be significant, as the density of the B<sub>4</sub>C was much lower than that of the Ru. Comparing the simulation parameters generated in the present work with Joy's database, it was found that the model and the input parameters used in the simulations were sufficiently accurate.

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## 1. Introduction

The secondary electron emission coefficient (SEEC) [1,2] of a material is an important factor that affects the image contrast that can be obtained from an electron microscope [3–9], as well as the degree of surface charging [9–12]. The SEEC is a physical constant, and so many researchers have analyzed this parameter based on constructing universal curves [1,2,13]. However, in actual applications, the surfaces of many materials are covered by a native oxide film and other sources of contamination owing to exposure to atmospheric air or various cleaning procedures, and the thicknesses of these layers vary depending on the cleaning procedure and the number of cycles applied [14,15]. Hence, considerations of the actual total electron yield (TEY) of a material should take into account the chemical compositions of the native oxide and any surface contamination as well as their respective thicknesses [16–18]. The density of a material is known to change depending on the quality of the film resulting from the particular deposi-

tion procedure employed [19–21]. Samuelsson et al. have reported that the densities of sputter-deposited films are 5–30% less than the bulk density values given in literature (corresponding to the theoretical densities) [21]. This density difference affects both the secondary electron (SE) yield ( $\delta$ ) and the backscattered electron (BSE) yield ( $\eta$ ) [22,23]. In the semiconductor industry, the presence of a native oxide film or contamination, as well as variations in the material density, can have a significant impact on various aspects of a product, such as fabrication yield and lifetime [24]. To control and improve the quality of such devices, electron beam (EB) testing techniques such as critical dimension metrology using scanning electron microscopy (SEM) [25] and defect inspection using EB inspection systems [4–10,26,27] are widely used. The TEY is one of the most important factors to consider when optimizing testing parameters such as incident beam energy (the landing energy of the primary electrons [PEs]) and beam current [4–9,26,27]. However, in the case of insulator materials, the true TEY is difficult to measure owing to surface charging [28], because the SE signals vary during EB irradiation [29,30]. Hence, the assessments of TEY variations are often complicated by the surface charging effect [12].

In the present work, to better understand the TEY variations, the individual effects of a native oxide film, surface contamination

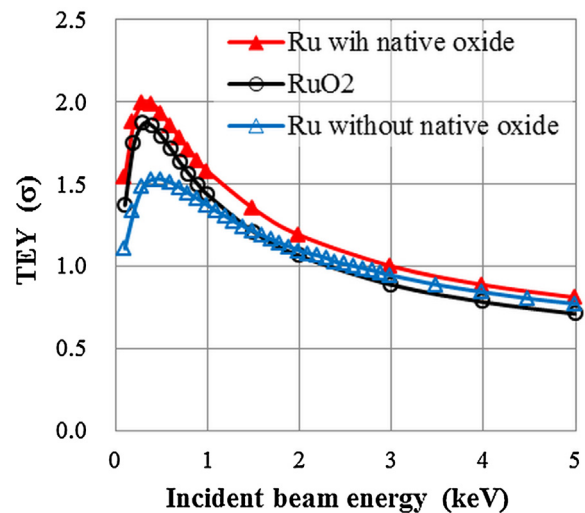
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and material density changes on the TEY were investigated in the absence of the surface charging effect. For this purpose, we focused on two materials: Ru and B<sub>4</sub>C. Ru is widely used in the semiconductor industry as a capping layer for extreme ultraviolet (EUV) reflective multilayers in EUV masks [4,6–8,24]. Both RuO<sub>2</sub> and RuO<sub>4</sub> are known to occur as native oxides. However, because RuO<sub>4</sub> is easily removed with water, only the RuO<sub>2</sub> film is left behind after the cleaning procedure [14,15]. RuO<sub>2</sub> is also known to be a conductive material [31–33], and hence it does not produce a surface charging effect. B<sub>4</sub>C is also a conductive material [5,9,24], and generates very little native oxide, B<sub>2</sub>O<sub>3</sub>, because this oxide only forms above 800 °C [34]. In fact we have already reported that the charging effect for 100-nm-thick B<sub>4</sub>C is negligible [9]. Hence, variations in the TEY solely resulting from surface contamination can be investigated in the absence of both surface charging and a native oxide film by using B<sub>4</sub>C. Therefore, in this study, the effects of native oxide, surface contamination and material density on the TEY were examined by studying Ru and B<sub>4</sub>C.

## 2. Experimental

Ru, RuO<sub>2</sub>, and B<sub>4</sub>C layers (100 nm thick) were deposited on Si substrates by magnetron sputtering at room temperature [35,36]. The TEYs ( $\sigma = \delta + \eta$ ) of these samples were measured using a scanning Auger microscope (SAM) (PHI, Scanning Auger Microprobe Model 4300) with a specially designed sample holder incorporating a Faraday-cup attachment in an ultra-high vacuum environment at  $5 \times 10^{-8}$  Pa. The scanning area was  $500 \times 400 \mu\text{m}$  and the scan speed was 0.2 s per scanning area. The incident beam current was fixed at 50 pA. Although the beam diameter varied depending on the beam energy, the diameter at 100 eV was estimated to be approximately 20  $\mu\text{m}$ . The deleterious effects of variations in the diameter with changes in beam energy on the measurement accuracy were minimized by continuously scanning the measurement area during the acquisition of each data set. To avoid any damage or oxidation during to cleaning process, the as-deposited samples were installed in the vacuum chamber without being cleaned. Details of the SAM configuration and TEY measurement method used in this study have been described elsewhere [37]. The TEY values of Ru with and without a native oxide film and the TEY of B<sub>4</sub>C with and without surface contamination were measured. To remove the native oxide coating and any surface contamination, the surfaces of the Ru and B<sub>4</sub>C samples were sputtered with Ar prior to assessing their TEYs. In general, when the surface of a compound material such as RuO<sub>2</sub> is sputtered, the heavier element is segregated on the surface because the lighter material is selectively sputtered. However, in the case of B<sub>4</sub>C, because the densities of B and C are very close, this segregation effect is minimized. The composition and thickness of the native oxide and contamination were analyzed by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The effect of the native oxide film, the surface contamination and the film density on the TEY were determined by generating TEY curves using the Monte Carlo simulation process developed by Ohya et al [38,39]. In this simulation method, the SE emission is generally modelled in three steps: SE generation in the solid, transport of the SEs to the surface and their escape over a surface barrier. Four parameters were used to fit the experimentally obtained TEY curves. These were the effective energy required to produce an SE ( $\varepsilon$ ), the effective SE escape depth ( $\lambda$ ), the probability of electrons escaping from the surface through the surface potential barrier (P) and the density of the material (N). The parameters  $\varepsilon$  and  $\lambda$  can be validated by comparing them to values previously reported by Joy et al. [2]. The effects of the surface potential barrier, such as the work function and electron affinity, on the TEY can be simply represented by the parameter P. Moreover,



**Fig. 1.** Experimentally-obtained total electron yield (TEY) values for Ru with native oxide (“as-deposited” condition), RuO<sub>2</sub> and Ru without native oxide (following Ar sputtering).

the influence of the penetration depth of PEs and the BSE yield on the TEY can be evaluated by changing the material densities. This semi-empirical model allows assessment of the effect of surface and bulk conditions on the electron emission. Details of this Monte Carlo model have been previously published [27,38,39].

## 3. Results and discussion

### 3.1. Impact of native oxide and material density on TEY

Fig. 1 shows the experimentally-obtained TEY curves for Ru before and after Ar sputtering and of RuO<sub>2</sub> before sputtering, all as functions of incident beam energy. The maximum yield,  $\sigma^m$ , obtained from the RuO<sub>2</sub> is much larger than that from the Ru without the native oxide. However, these TEY curves intersect at 1.5 keV, after which (over the range from 1.5 to 5 keV), the yield from the RuO<sub>2</sub> becomes lower than that from the Ru. Many researchers have reported that the  $\sigma^m$  of an oxide will be much larger than that of the original metal [1,11,12], and two reasons for this effect have been proposed; the Malter effect [40] and a low energy barrier [41,42]. According to the Malter effect, if the oxide material is an insulator and the surface is positively charged, the positive charge will produce a high electric field in the insulator and this will pull more electrons from further beneath the surface. Thus the electron emission is caused by field emission at the bulk material through the insulating layer [1,40]. However, in the case of Ru and RuO<sub>2</sub>, because these materials are conductive (their measured resistivity values are  $7.0 \times 10^{-5}$  and  $2.8 \times 10^{-4} \Omega\text{cm}$ , respectively), the charging effect and the Malter effect are negligible. Therefore, the large TEY associated with the oxide material may be explained based on the energy barrier that inhibits electron escape from the sample surface [41,42]. The different energy barriers of Ru and RuO<sub>2</sub> can be experimentally verified from their SE energy distributions. Palmberg has reported that the peak energy of the distribution,  $E_{SE}^m$ , and the full width at half maximum (FWHM) both decrease with decreases in the surface potential barrier [43]. Fig. 2 shows the energy distributions emitted from the Ru samples as measured by AES [1,42]. The  $E_{SE}^m$  in the case of RuO<sub>2</sub> (5.1 eV) is lower than that for Ru (6.0 eV). Moreover, the FWHM for RuO<sub>2</sub> (13.5 eV) is smaller than that for Ru (15.2 eV). These results indicate that a lesser amount of energy is required for electrons to escape from the RuO<sub>2</sub> compared with the Ru. Furthermore, the Ru with native oxide generates the lowest  $E_{SE}^m$  and FWHM values (3.9 and 8.5 eV,

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