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Investigation of proximity effects in electron microscopy and lithography

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A fundamental challenge in lithographic and microscopic techniques employing focused electron beams are so-called proximity effects due to unintended electron emission and scattering in the sample. Herein, we apply a method that allows for visualizing electron induced surface modifications on a SiN substrate covered with a thin native oxide layer by means of iron deposits. Conventional wisdom holds that by using thin membranes proximity effects can be effectively reduced. We demonstrate that, contrary to the expectation, these can be indeed larger on a 200 nm SiN-membrane than on the respective bulk substrate due to charging effects. © 2012 American Institute of Physics. [doi:10.1063/1.3681593]

A major challenge in nanotechnology still is the fabrication of arbitrarily shaped nanostructures at predefined positions and with tailored chemical composition. One suitable and “clean” tool to manipulate matter very locally is a focused electron beam, with a diameter in the low nanometer regime. In order to apply this tool effectively, a deep understanding of the interaction of electrons with solid matter is required. Important processes in this context are elastic and inelastic scattering of primary electrons (PEs), leading to the emission of backscattered electrons (BSEs) and secondary electrons (SEs) in surface regions beyond the initial electron impact point. Another important issue is that electrons may alter the probed sample, e.g., by triggering displacement of atoms¹ or by inducing chemical processes.² Lithographic methods based on such electron induced chemical modifications can be subsumed as focused electron beam induced processing (FEBIP). One of these techniques is the electron beam induced deposition (EBID);^{3–6} it relies on the local electron beam induced dissociation of adsorbed precursor molecules, with the nonvolatile fragments forming the targeted deposit. Since recently, EBID is used in semiconductor industry to repair lithographic masks.⁷ One of the challenges in EBID are the so-called proximity effects, i.e., the scattering and the secondary emission of electrons, which lead to an effective broadening of the deposits compared to the diameter of the primary beam.⁴ The BSE proximity effect^{7–10} is caused by BSEs and the thereby induced SEs, while the forward scattered electron (FSE) proximity effect^{11–13} originates from scattering within an already produced deposit; both effects can cause deposition of material away from the PE impact area. In EBID, there is always a superposition of FSE and BSE proximity effects, i.e., these proximity effects cannot be studied separately. A common strategy to diminish the BSE proximity effect in EBID is to reduce the electron interaction volume by using thin membranes. With this approach and by applying low electron doses, extremely small deposits could be realized.^{14–17}

With electron beam induced surface activation (EBISA), we have recently introduced a FEBIP technique, where no

FSE proximity effect occurs.^{18,19} Figure 1 schematically depicts the ideal two step EBISA process: In the first step, the surface is irradiated and thereby locally activated with a focused electron beam; in the second step, it is exposed to the precursor iron pentacarbonyl, Fe(CO)₅. On the activated sites, which are identified as oxygen vacancies, i.e., understoichiometric silica,¹⁹ decomposition of Fe(CO)₅ at room temperature leads to the formation of Fe nuclei, which then grow autocatalytically upon prolonged precursor dosage to form clean, cubic Fe crystals,^{18,19} corresponding to bcc α -Fe.^{17,20} Therefore, EBISA can be exploited as a method to mark the position of electron induced modifications. As the deposits are formed after and not during electron beam irradiation, it is perfectly suited to study the BSE proximity effect without the superposed FSE proximity effect.

The aim of our study was to investigate the BSE proximity effect by comparing deposits prepared using EBISA on a thin silicon nitride (SiN) membrane and a bulk sample. The SiN membrane had a thickness of 200 nm (referred to as SiN-200 nm) and the bulk substrate was a Si crystal covered with a 50 nm thick silicon nitride layer (referred to as SiN-bulk). Since both were stored under ambient conditions for a prolonged time, they are covered by a native silicon oxide film, with a thickness in the order of 1 nm,²² i.e., both have the same surface properties.

In a first step, the BSE exit area and the corresponding proximity effect are estimated using Monte Carlo (MC) simulations. In Fig. 2, the results of a MC simulation performed with the program *Casino V 2.42* (Ref. 21) are depicted for both samples. In Fig. 2, the number of BSEs, emitted from the surface, is plotted vs. distance (radius), r , from the electron beam impact point. Overall, the total number of BSEs, which is expressed by the BSE coefficient η , is significantly reduced for the membrane, i.e., from $\sim 17.1\%$ (SiN-bulk) to $\sim 3.4\%$ (SiN-200 nm). Also, the radius of the BSE exit area, which is estimated as containing 99.99% of the emitted BSEs, is smaller on the membrane (blue, $\sim 1.5 \mu\text{m}$) as compared to the bulk substrate (red, $\sim 2.2 \mu\text{m}$). The simulation therefore indicates that the BSE proximity effect should indeed be significantly smaller on the membrane than on the bulk sample.

Figure 3 depicts iron deposits fabricated on the two samples by EBISA with two different electron doses (6 and

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FIG. 1. (Color online) Scheme of the ideal EBISA process: (a) local irradiation of the surface with a focused electron beam; (b) dosage of the precursor and adsorption on the surface, dissociation of molecules at the activated sites; (c) formation of Fe nuclei; (d) autocatalytic decomposition at the initial Fe nuclei; (e) enlarged, autocatalytically grown Fe deposit.

720 nC) and subsequent autocatalytic growth (cf. Fig. 1). The resulting clean iron deposits exhibit a crystalline shape (see, e.g., inset in Fig. 3(c)). This result demonstrates that the EBISA concept can also be applied to natively oxidized SiN surfaces.^{18,19} Since the iron deposits on both samples are expected to be very similar, the contrast of the different images was set such that they appear with similar brightness. The darker appearance of SiN-200 nm compared to SiN-bulk then is in line with the simulated lower BSE coefficient of the membrane.

Comparing the size of all iron deposits with the size of the electron beam (~ 3 nm diameter), it is obvious that they are extremely enlarged due to proximity effects. The deposit radius for the lower electron dose (6 nC) is ~ 0.45 μm on the membrane compared to ~ 1.65 μm on the bulk substrate (see supplementary material for applied radius evaluation³¹).

Assuming the BSE proximity effect as a main source, this experimental result reflects the trend expected from literature⁴ and from the MC simulations, depicted in Fig. 2.

A completely different and unexpected behavior is observed for the high electron dose: the deposit on the membrane is now larger than on the bulk substrate (cf. Figs. 3(c) and 3(d)). This contradicts the expectation solely considering electron scattering as the source of the broadening. While the deposits on SiN-bulk have a rather defined edge, they exhibit a fuzzy boundary on the membrane, consisting of scattered bright spots, which are identified as individual crystallites. This behavior makes a direct measurement of the radius difficult; we therefore, use the grey values of the SEM

image and estimate the radius as the distance from center where the integrated intensity profile has dropped to 10% of the maximum value (see supplementary material for applied radius evaluation³¹). Using this approach, we obtain a radius of 5.84 μm for the iron deposit on the membrane in Fig. 3(c). Note that individual scattered particles can still be found at larger distances from the original electron beam impact point.

The radius of the high dose deposit on the bulk substrate in Fig. 3(d) is determined to be 2.85 μm and thus exceeds the value of 2.2 μm from the simulation by a factor of 1.3. This deviation is attributed to a general underestimation of the radius by the simulation, which does not include secondary processes like Auger electron emission and also uses an energy cutoff at 50 eV. Due to the latter, electrons with lower energies are omitted, although they are expected to account for some electron induced processes, e.g., oxygen desorption.²³ Considering these limitations of the simulation, the observed deposit size on the bulk substrate can be explained by the BSE proximity effect. When comparing the radius of 5.84 μm of the high dose deposit on the membrane to the simulated value of 1.5 μm (Fig. 2), it is evident that this value is too large to be explained by the BSE proximity effect.

To gain further insight, the area of the iron deposits on both substrates was analyzed for different electron doses. While the deposit area on the bulk substrate saturates at a value close to the simulated BSE exit area, on the membrane interestingly a linear dependence is found (see

FIG. 2. (Color online) Monte Carlo simulation of BSE exit area with the program Casino V2.42: BSEs emitted from the surface plotted vs. the radius, with 0 being the impact point of the PE beam, for the SiN-bulk and the SiN-200 nm substrate. The BSE hits are sampled in 20 nm increments and correspond to an exit annulus with $A = [(n \times 20 \text{ nm})^2 - ((n-1) \times 20 \text{ nm})^2]\pi$ and $r = (n-1) \times 20 \text{ nm}$ ($n \in \mathbb{N}$); the hits are not normalized to this annulus.

FIG. 3. (Color online) SEM images of Fe deposits on SiN-200 nm ((a) and (c)) and on SiN-bulk ((b) and (d)) generated via EBISA and successive autocatalytic growth via 6 ((a) and (b)) and 720 nC ((c) and (d)) (point irradiation at $I_{\text{PE}} = 400$ pA and $U_{\text{PE}} = 15$ kV) and an additional gas dosage time of 270 min at a nominal $\text{Fe}(\text{CO})_5$ background pressure of 3.0×10^{-7} mbar.

supplementary material for corresponding data³¹). The latter observation for the membrane suggests a correlation of the deposit area with the impinging number of electrons, i.e., charging appears likely to contribute. Generally, the bombardment of an insulating thin membrane with high energy electrons yields positive charging.²⁴ We could indeed confirm this, e.g., by shifts of the characteristic Fe LMM peaks by 220 eV to lower kinetic energy in Auger electron spectroscopy (AES) of corresponding iron deposits on the SiN-200 nm membrane.

To be able to further interpret these results, it is crucial to clarify the nature of the surface activation. Recently, we demonstrated that the active sites on SiO_x are oxygen vacancies generated by electron stimulated desorption.^{18,19} This mechanism is also confirmed for the here investigated membrane covered with a native silicon oxide: it was found that a pre-irradiated membrane remains active towards Fe(CO)₅ decomposition for at least one day, with no significant differences of the observed iron deposits. This is a strong indication for a chemical modification (i.e., activation); if simple charging were to play a role, the activity should have decayed after one day. Furthermore, electron beam induced oxygen depletion in electron irradiated regions was confirmed by AES on the SiN-bulk substrate (not shown), similar to our results on SiO₂.^{19,25}

In the following, we propose a mechanism for the unexpected broadening of the EBISA deposits on the membrane: In a first step, electrons are ejected upon high energy electron irradiation, mainly due to SE emission. In a second step, the resulting holes accumulate at the SiO₂/Si₃N₄ interface, which is a Si-enriched silicon oxynitride with a thickness of ~0.6–0.8 nm,^{26,27} and which is well known to trap charges.^{26–29} Due to the Si enrichment, the interface should be more conductive than the SiO₂ or the Si₃N₄ layer. Therefore, a radial transport of the holes along this Si-enriched interface occurs, even to areas beyond BSE emission. The linear increase of the deposit area with the applied electron dose can be explained by a simple diffusion model combined with Coulomb repulsion. Thereby, the positively charged holes, which initially have the highest density close to electron beam impact point, are the driving force for their outwards motion. Along the way, electron transfer (ET) from oxygen to Si⁺ occurs, which finally leads to the formation and desorption of O⁺ species (in analogy to the Knotek-Feibelman mechanism^{23,30}). As soon as one oxygen is consumed per SiO₂ (i.e., SiO is formed¹⁹), the holes have to travel further for neutralization. This behavior induces a radial spread of the holes and explains the linear growth of the deposit area with electron dose.

Finally, we considered and ruled out other mechanisms for surface activation, such as electron beam induced heating, backscattering of electrons from underneath the membrane, and bending of the membrane.

We report on a not yet described proximity effect on a SiN-membrane covered with a thin native SiO₂ layer in electron microscopy. The observation of a strong broadening of the EBISA deposit at high electron dose, which is beyond the expected BSE proximity effect, is interpreted as being due to the positive charging of the membrane and the thereby induced oxygen desorption: After electron ejection, the

resulting holes accumulate at the SiO₂/Si₃N₄ interface. Due to its conductivity, radial transport of the holes along interface occurs, driven by repulsive Coulomb interactions. Finally, electron transfer from oxygen to Si⁺ leads to the formation and desorption of O⁺ species.

The applied electron doses might be higher than the ones applied in standard lithography; however, they are easily obtained during imaging or when performing chemical analysis. It is suggested that when using thin SiN-membranes in combination with an electron beam, it should be considered that this process may alter the chemical and/or physical properties of the sample in regions which may exceed by far the PE beam diameter and the area where electrons are scattered.

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