Reflectivity of super slow electrons from clean and oxidized steel surface

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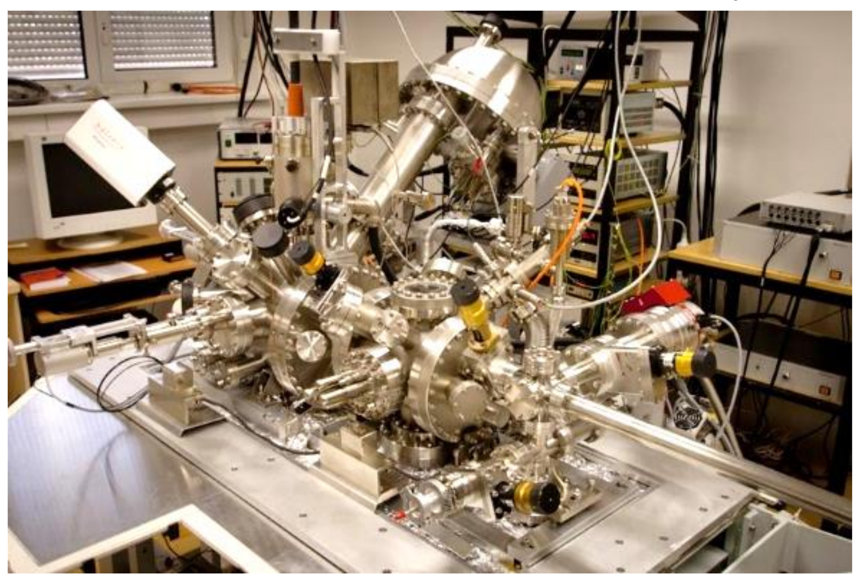
The recent trend in scanning electron microscopy (SEM) is to focus on using very low landing energies of the primary electrons. Modern instruments are equipped with a beam deceleration mode, which enables users to operate the commercial SEM at energies of tens or even units of eV. Using low landing energies is inseparably connected with increasing surface sensitivity, hence the surface conditions (e.g. presence/absence of native oxide, contamination, … etc.) start to play very important role in the image formation. Contrast in SEM micrographs obtained at tens or even units of eV is very difficult to interpret, especially in the case of "real" specimens that do not have perfectly defined surface. For instance, metals and alloys becomes naturally covered by a thin native oxide layer and several other contaminants after air-exposure. Thus, it is hard to interpret the contrast mechanism and consider the effect of the surface condition on the contrast in the micrographs at low landing energies, at which the surface condition plays the most important role in the image formation. In this study, we present steel characterization by the electrons of various landing energies, namely from 5 keV down to 0 eV. We demonstrate that the primary electrons of very low landing energy exhibit high sensitivity to grain orientations (observed even through the native oxide at the ultra-low landing energy) and are able to image the surface potential differences.

UHV SLEEM

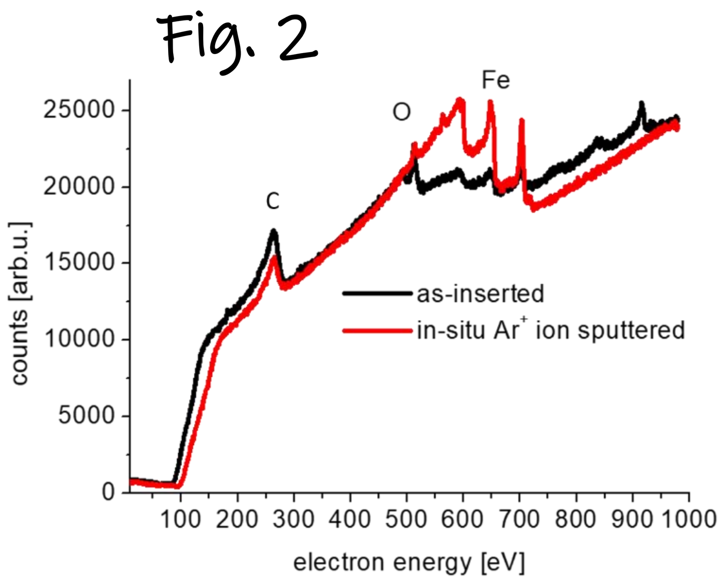
Fig. 1



The specimen was characterized by an in-house designed ultra-high vacuum scanning low energy electron microscope (UHV SLEEM, Fig. 1). The UHV SLEEM instrument consists of the main chamber, the preparation chamber and the sample loading chamber. The preparatory chamber allows sample surface cleaning by means of argon ion sputtering and electron bombardment heating, which enables us to perform in-situ cleaning of specimen surfaces and to remove a native oxide and contamination layers. Part of the specimen surface was in-situ cleaned in the preparation chamber of the UHV SLEEM instrument. The following settings were used for the Ar^+ ion sputtering process: ion beam energy 5 kV, angle of incidence 5 degrees relative to the sample surface, duration of treatment 45 minutes, spot size on the tilted specimen 1.1 x 2.4 mm, stationary beam (no scanning), ion beam current 10 μA.

Surface treatment

Fig. 2



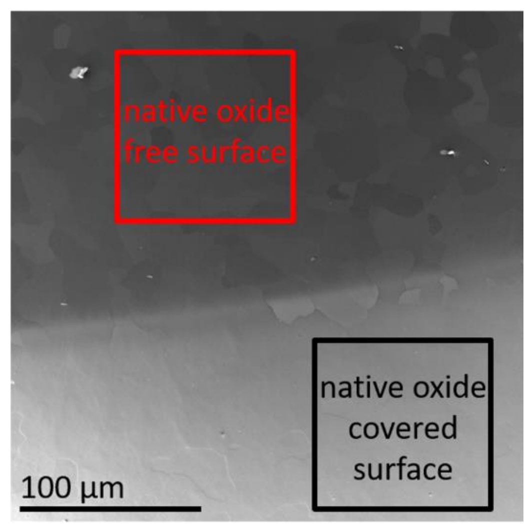
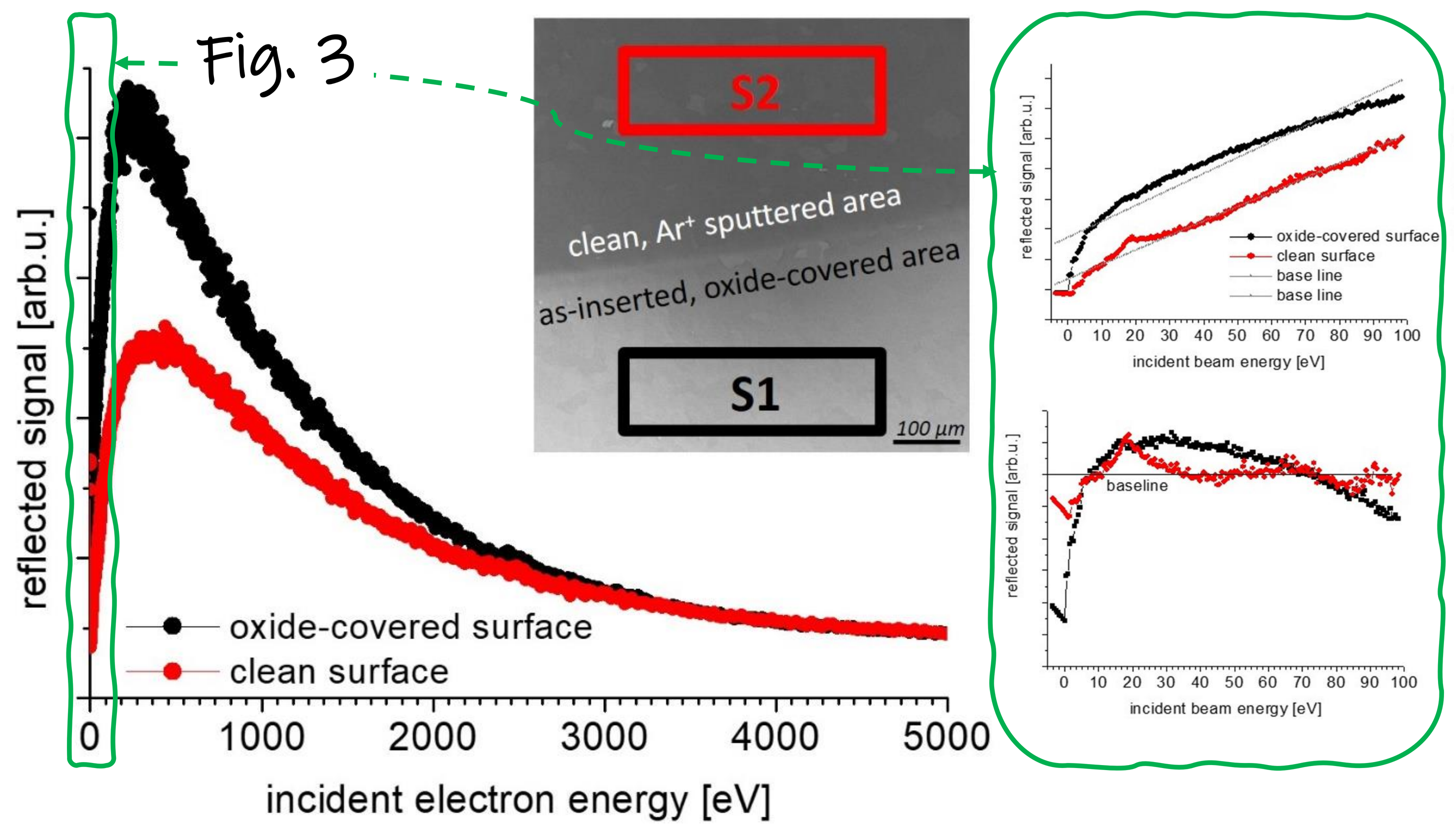


Fig. 2 shows a SLEEM micrograph of the interface between the Ar^+ ion beam sputtered and the native-oxide-covered locations, together with the corresponding Auger spectra collected from the areas marked in the SLEEM image. The Auger spectra were measured inside the main chamber, i.e., after the transport of the specimen from the preparation to the main chamber

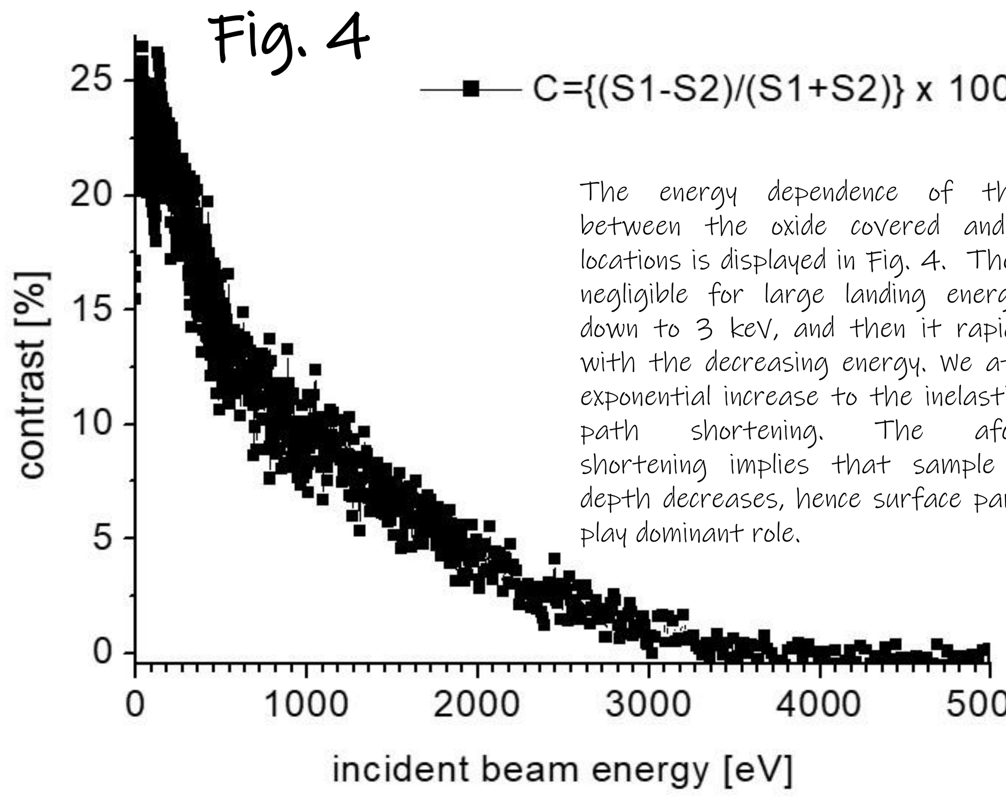
Penetrability of a native oxide layer by electrons

Fig. 3



The observation area contains both Ar^+ ion sputtere and as-inserted locations, see SLEEM micrograph inse in Fig. 3 – marked areas S1 and S2, each well withi the two differently treated surfaces parts. Th landing energy was varied automatically by means c the specimen bias with a primary beam energy fixed a value 6 keV. The micrographs were collected wit identical brightness and contrast settings, whic enables direct comparison among them. Two differen steps in the landing energy have been used to obtai the images; 0.5 eV within the range from 100 eV to keV and the already mentioned minimal step ≃ 0.3 e for landing energy less than 100 eV. Dependence c average signal collected from each of the two areas c interest on incident electron beam energy is presente in Fig. 3. We use the data to calculate correspondin contrast C= {(S1-S2)/(S1+S2)}x100 [%], where S1 i the image signal averaged over the location situate inside the area covered by the native oxide layer an S2 is the image signal averaged over the locatic inside the Ar^+ ion sputtered area.

Fig. 4



The energy dependence of the contrast between the oxide covered and oxide free locations is displayed in Fig. 4. The contrast is negligible for large landing energies, roughly down to 3 keV, and then it rapidly increases with the decreasing energy. We attribute the exponential increase to the inelastic mean free path shortening. The aforementioned shortening implies that sample penetration depth decreases, hence surface part starts to play dominant role.

DFT calculations

Fig. 5

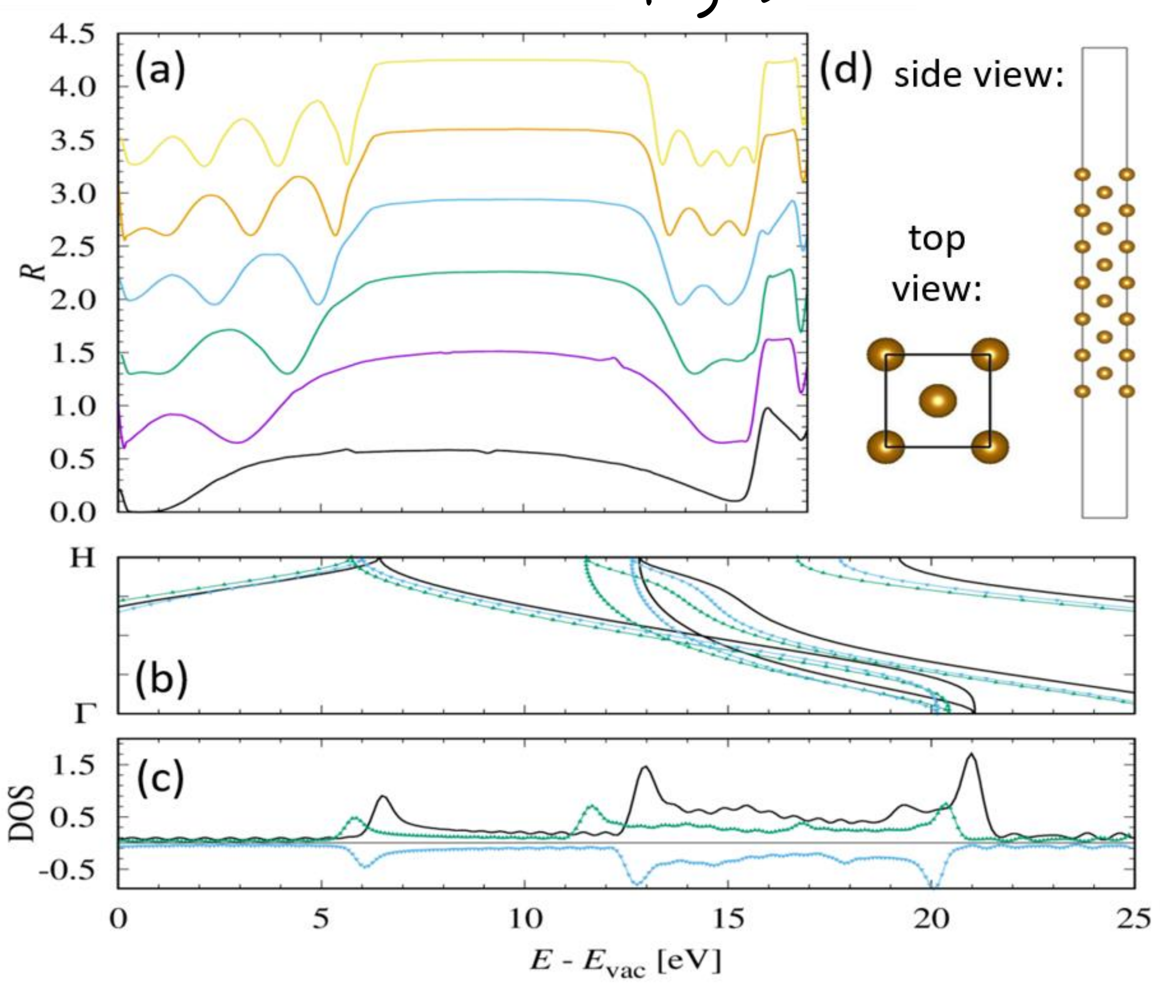


Fig. 5 Normal incidence reflectivity from 3 to 13 atomic layers for free standing Fe-BCC(001) slab, bottom to top. The simulated data are shifted by 0.6 for better visual presentation (a); band-structure of bulk Fe-BCC along the reciprocal path described in vertical axis – spin unresolved (solid line without any symbols, black), spin-up (upward pointing triangles, green), spin-down (downward pointing triangles, blue) (b), bulk DOS corresponding to the band-structure with zero indicated by a vertical line. The symbols and colors used are the same as in (b) and spin-down DOS was multiplied by -1. (c); visualization of the slab supercell generated using the software VESTA is included (d). All horizontal (energy) axis are aligned with the one displayed in the case of DOS results in segment (c).

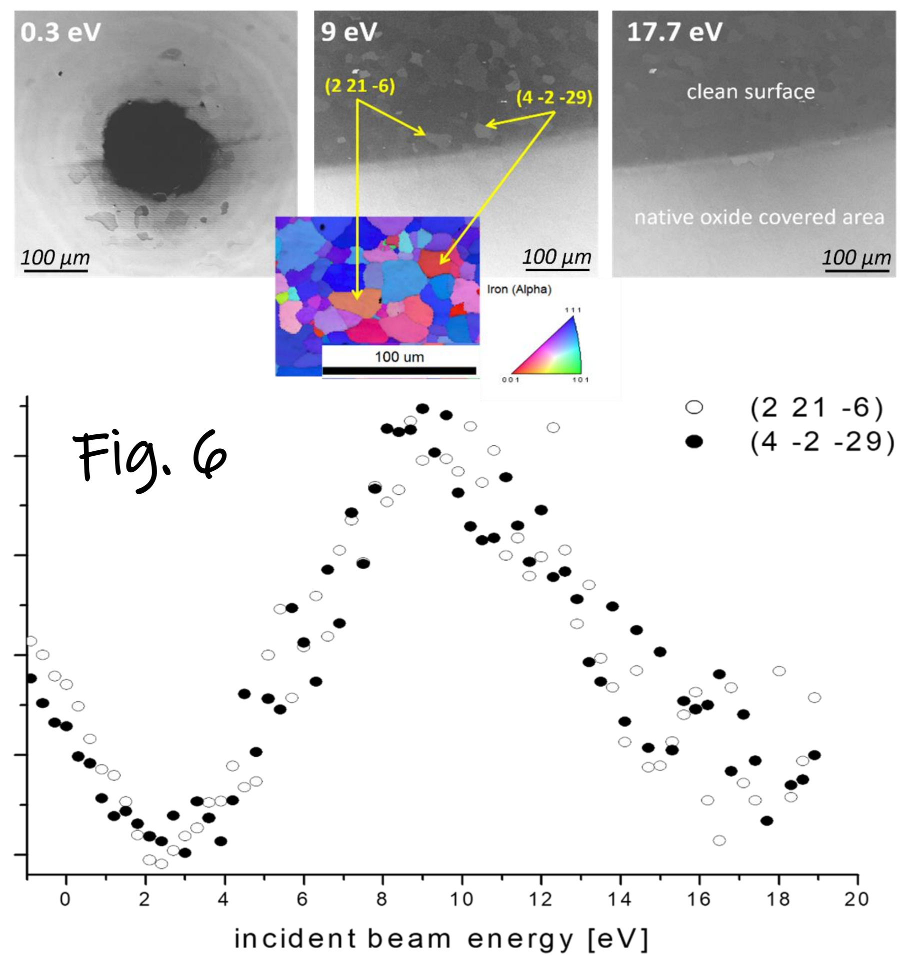
Sensitivity of very slow electrons to the local electronic structure

Fig. 6 Reflected signal from the Fe grains with average crystallographic orientation of (2 21 -6) and (4 -2 -29) after linear baseline subtraction, together with corresponding UHV SLEEM micrographs obtained at 0.3 eV, 9 eV, and 17,7 eV and the EBSD orientation + phase map containing the investigated grains. Position of the grains is marked in the UHV SLEEM micrograph acquired at 9 eV landing energy (middle-top inset of this figure).

As is clearly visible, both curves have a broad significant peak centered at 9 eV. Hence, the UHV SLEEM data are in a very good agreement with the DFT calculated results, Fig. 5(a)+(c).

The reflectivity data exhibit a subsidiary peak at approximately 16 eV. This agrees with the DFT calculated reflectivities in Fig. 5(a). The 2nd major theoretical peak is higher than the corresponding experimental one. Inclusion of the inelastic effects would decrease the height of this theoretical peak.

Fig. 6



Near zero landing energies in SEM

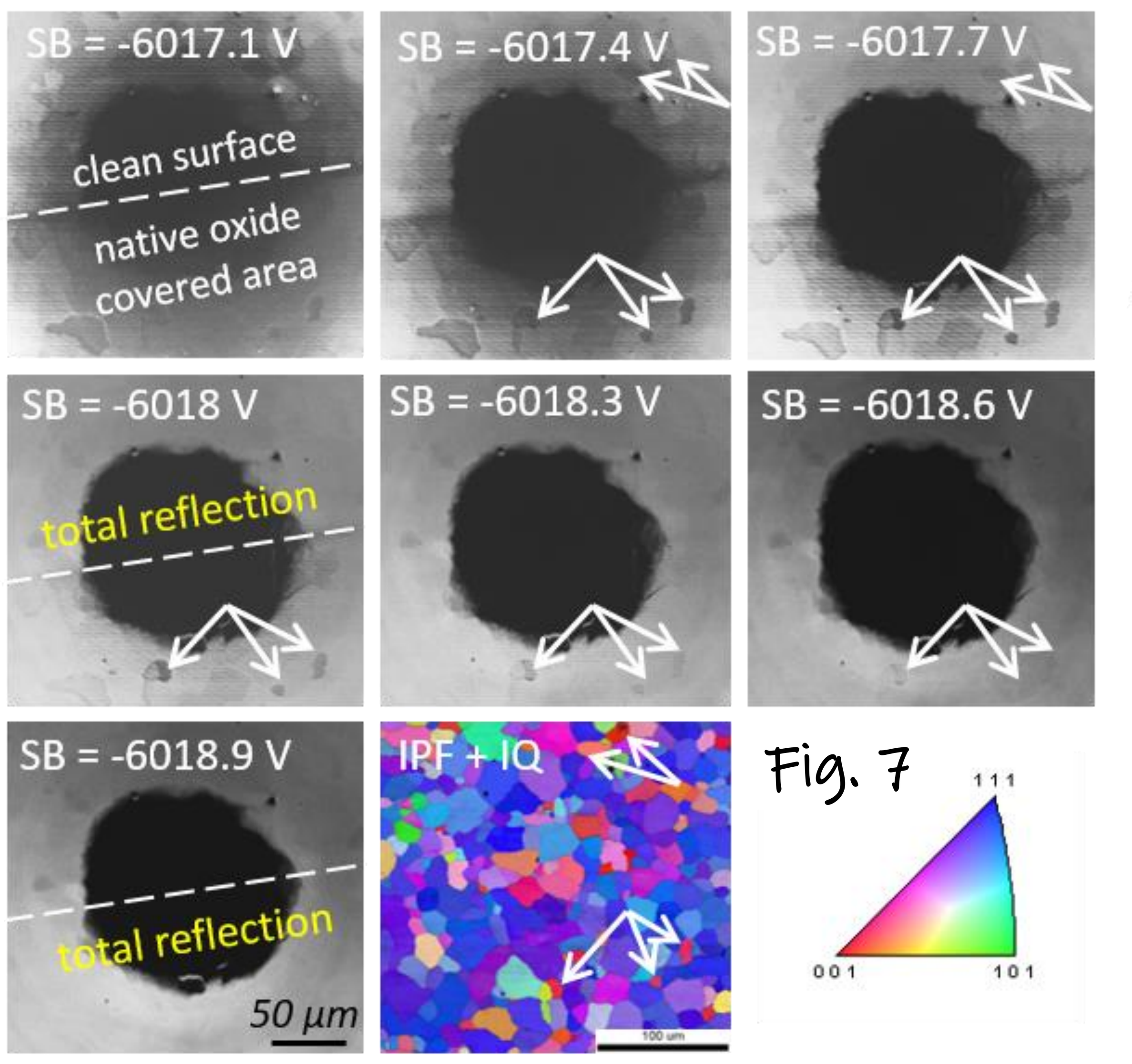


Fig. 7

Let us compare the reflected signal from the native oxide covered area and the area without the native oxide covering in the case of super slow electrons having the landing energy close to the mirror condition. As mentioned above, the final landing energy of the primary electrons is controlled by the specimen bias. Fig. 7 shows a series of the UHV SLEEM micrographs obtained at landing energies ± 0.9 eV from the mirror condition for the clean surface. The fading of two grains marked in Fig. 7 at different energies demonstrates that the native oxide covered area reaches the mirror mode at higher values of the specimen bias. As reported already by Aoyama et. al, the super slow electrons are sensitive to the surface potential differences caused by the differences in the work function. The results presented in Fig. 7 indicate lowering of work function about 1 eV on the naturally oxidized part of the specimen. Considering oxygen and CO contamination only demonstrate that oxidation of Fe (001) surface results in increase of the work function by ~ 1.0 eV.

Conclusion

The paper has examined and compared the reflectivity of electrons from the clean and native oxide covered mild steel surface. The mild steel was characterized by the in-house designed UHV SLEEM. Backscattered signal was recorded from the clean and the oxidized surface in the energy range from 0 eV to 5 keV. The main results of this paper are summarized below.

- The contrast between the native oxide covered and the native oxide free surface, Fig. 3, is negligible from the maximal energy 5 keV to roughly 3 keV and then it starts to increase exponentially with the landing energy decreasing further.
- The very slow electrons (< 40 eV) are sensitive to the local electronic structure. The grains with the orientation close to (001) show very good agreement between the measured reflected signal, Fig. 6, from the UHV SLEEM micrographs and the reflectivity predicted from our DFT calculations, Fig. 5.
- The super slow electrons (i.e. electrons having the landing energy close to the mirror condition) are able to image the surface potential differences caused by the differences in the work function, see Fig. 7. Presence of the air-formed native oxide on the mild steel surface, with chemisorbed H_2O and OH groups, decreases the surface work function.
- The iron grains having the orientation close to (001) show the specific contrast w.r.t. other orientations at near zero landing energies of the primary beam. This contrast is retained even though the native oxide film was present.

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