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Background Effects in ESDIAD Measurements on Si(111)-(7x7)

by

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I. Introduction

The imaging of the angular distribution of desorbing ions and excited neutral species, produced by electron stimulated desorption, has been accomplished with the electron stimulated desorption ion angular distribution (ESDIAD) technique, first devised by Czyzewski, Madey, and Yates in 1974.[1] Electron stimulated desorption causes positive-ion fragments, negative-ion fragments, neutral, and excited neutral (metastable) species to desorb from adsorbates. The trajectory of these desorbed species is closely related to bonding directions present on a single crystal surface.[2-4]

In addition to these ionic and neutral species, characteristic x-rays are also produced in the electron bombardment of the crystal and these photons contribute to a background signal during the ESDIAD measurement. This background signal was first reported by Niehus and Krahl-Urban on single crystal Mo(100) using time-of-flight measurements.[5] Recent improved methods in the ESDIAD measurement technique permit the elimination of the background signal through digital acquisition, storage, and subtraction.[6,7] The enhanced digital ESDIAD technique has been applied successfully to a number of adsorbate-metal and adsorbate-oxide systems.[8,9] Only recently has the ESDIAD technique been applied to adsorbate-semiconductor systems.[10-13]

In this work, we describe the background effect from the ESDIAD study of the Si(111)-(7x7) surface and the importance of the elimination of the background signal in the study of the ion angular distribution from clean and H-exposed Si(111) surfaces. We find that the background intensity varies linearly with incident electron beam energy and current density and is consistent with the production of characteristic soft x-rays from electron bombardment of Si.

II. Experiment

The ESDIAD measurements were performed in a ultrahigh vacuum (UHV) chamber (base pressure = 4×10^{-11} Torr) and is described in detail elsewhere.[14] The ESDIAD apparatus, shown in Fig. 1, is equipped with a Comstock EG-401 electron gun and x-y deflection plates. The typical electron beam energies used to produce the patterns reported here are 300-500 eV with currents of ~10 nA in a 1 mm diameter spot. The electron beam is delivered to the crystal through a grounded drift tube which penetrates the hemispherical grids of the retarding field analyzer (RFA). The entire RFA assembly is shielded as shown in Fig. 1 with μ-metal and stainless steel.

The grids, numbered in order of increasing distance from the Si crystal, are biased for ESDIAD measurements of positive ions as follows: $G_1=G_2=0$ V, $G_3=(0.7)V_{xtal}$, $G_4=0$ V, and $G_5=-500$ V. The grid G_5 is biased to retard any scattered electrons (and possible ESD-produced negative ions) from the Si surface and to accelerate the positive ESD-produced ions to the microchannel plate (MCP)/anode collector assembly. For all ESDIAD measurements reported here, the Si(111) crystal is biased at $V_{xtal}=+100$ V and the crystal temperature is T = 120 K. All other stray electron sources (e.g. ion gauge, quadrupole mass spectrometer ionization source, etc.) are turned off during ESDIAD measurements. With the RFA at these potentials, positive ions, neutral species, and soft x-rays, produced from the ESD process, are collected by the MCP/anode assembly and the resultant signal is stored in a digital acquisition system described previously.[7]

To obtain the background signal due to the characteristic soft x-rays and neutral species, the positive potential of the retarding grid, G_3, is increased to $G_3=(1.5)V_{xtal}$. Thus all positive ions are retarded and only the signals from x-rays and neutral species will be recorded.

The apparatus can be switched to a low-energy electron diffraction (LEED) mode by simply changing the grid potentials to detect elastically scattered electrons.[14]

The Si(111) crystal (1.30x1.31x0.15 cm) was Czochralski grown, p-type Boron doped (nominal resistivity= 10 Ω-cm) material. The crystal was cut from a commercially polished wafer, slotted for mounting, and chemically cleaned prior to insertion into the UHV chamber.[14] Final preparation in UHV was accomplished by 3 keV Ar^+ ion sputtering at glancing incidence (1.8 μA cm^{-2} for 15 min.) and annealing to 1173 K, followed by a slow cooling (<5 K/s) to 120 K. LEED patterns from this procedure show a sharp (7x7) pattern. The crystal is mounted on a rotary manipulator and can be rotated to a number of instruments in the UHV chamber for analysis.[14] In particular, crystal cleanliness was established with a scanning Auger spectrometer and no evidence for impurities (for example: C, N, O, Ni) was seen for atomic concentrations above 0.01 within the depth of sampling.

The chamber was equipped with a W-spiral filament for the production of atomic H species for hydrogen exposures. The crystal was positioned about 4 cm from the hot W spiral which operated at a temperature of 1800 K. Crystal temperatures, determined from a thermocouple carefully inserted in the crystal[15], never exceed 340 K during exposure to the hot W spiral. The formation of $SiH_x(a)(x\leq3)$ species is observed to occur quite readily under these conditions.[16]

III. Results and Discussion

A. Dark current measurements

With the crystal rotated out of the electron beam, a dark current emission pattern is observed. This is shown in Fig. 2(a) where the x-y deflection plates have been grounded and no measurable electron current is produced at the sample position. The observed emission is located on the electron gun side of the ESDIAD analyzer (shown by the arrow in Fig. 2) and suggests that soft x-ray radiation from electron bombardment of lens elements inside the electron gun or UV radiation from the electron gun filament is responsible for the observed pattern despite the shielding surrounding the RFA. With the electron gun filament off, a very low intensity (<1% of typical ESDIAD pattern intensities) flat background is observed (not shown) and is therefore due to other spurious noise sources.

The effect of biasing the x-y deflection plates is shown in Fig. 2(b-d) (the crystal is rotated out of the electron beam). The potentials used on the deflection plates were established by maximizing the electron beam current to the crystal. The asymmetry in the x-y values were due to deflection plate placement at the end of the electron gun. The change in the observed emission as different deflection plates are biased indicates that the detailed delivery pathway for electrons to the system affects the intensity of the spurious background pattern, but not its general location. Since bombardment of the deflection plates occurs during typical ESDIAD measurements, these relatively small source-related signals must be eliminated for quantitative interpretations of the bonding directions of adsorbates.

B. Background effect on Si(111)

The raw ESDIAD pattern from a clean, prepared Si(111)-(7x7) crystal (biased at +100 V) is shown in Fig. 3(a). (All of the ESDIAD patterns shown herein have the same vertical scale.) A background pattern, in which all charged particles have been retarded by the RFA, is acquired with the crystal in position and is shown in Fig. 3(b). This background pattern is primarily due to characteristic soft x-ray emission from the Si surface, as will be shown. The true positive ion pattern from the clean Si(111) surface is shown in Fig. 3(c) and was produced by the subtraction of the background data (Fig. 3(b)) from the raw ESDIAD data (Fig. 3(a)), and 49-point smoothing to reduce noise.[7] The total yields represented in the patterns shown in Fig. 3(a) and (b) are of the order of $\sim 10^6$ counts. The processed data, shown in Fig. 3(c), has a total yield of $\sim 10^5$ counts: well above the noise level for our counting statistics ($\sqrt{n}$). Measurements of the clean prepared Si(111)-(7x7) surface, reported elsewhere[16], show that the observed ion signal from the "clean" Si(111) surface (Fig. 3(c)) is due to ESD-produced H^+ ions originating from residual surface hydrogen. This residual surface hydrogen is believed to originate from the bulk. The concentration of this residual surface hydrogen is estimated to be ≤ 0.1 monolayer, as determined by quantitative temperature programmed desorption measurements.[16]

The background pattern of Fig. 3(b) is quite typical of such measurements on the clean Si(111) surface. A depression in the background intensity is noted in the center of the pattern and may be a result of electron scattering from the cylindrically-symmetric RFA grid support rings or other such components, resulting in a circular soft x-ray pattern near the edge of the collector.

The raw ESDIAD pattern of Fig. 3(a) (which includes the background signal) also has a further attenuation on the electron gun side of the ESDIAD apparatus (electron gun side shown by the arrow). Such attenuation has been attributed to interference of the drift tube placement in the RFA with the emitted ESD ions.[7,12] Because the processed data (Fig. 3(c)) is a result of the background data subtraction from the raw ESDIAD data, a combination of these attenuation effects manifest themselves in the final (processed) pattern. Such attenuation effects may be more pronounced on surfaces exposed to an adsorbate (see below).[12]

The dependence of the background yield from a "clean", prepared Si(111) surface on the electron beam energy is shown in Fig. 4(a). The observed background yield in the 100 eV to 500 eV range is consistent with a soft characteristic x-ray emission from the silicon surface (and/or the grid support rings).[5,7,17] We note that the observed threshold for the background yield (~100 eV) is consistent with the excitation of the Si-2p transition (~102 eV), as measured in x-ray photoemission studies.[18]

Further evidence of a soft characteristic x-ray emission source is seen from the data of Fig. 4(b), where a linear dependence of the background yield with electron current density is observed. This also suggests that x-ray photons are primarily responsible for the observed background effects.[15] We note that the intercept of Fig. 4(b) (i.e. at an electron current density of zero) corresponds to a dark current signal of $\sim 5 \times 10^5$ counts for these measurements.

The background effect and the observed linear dependence of the background yield with electron beam energy and current density has been reported by Dresser, et al. for the clean Ni(110) surface.[7] Although their paper does not report a threshold energy for x-ray photon production, extrapolation of their incident electron energy dependence measurements (Fig. 6(b) of ref. 7) is consistent with the excitation of the Ni-3p transition (~70 eV) reported in the photoemission literature.[18]

C. ESDIAD measurements from atomic H-exposed Si(111)

The Si(111)-(7x7) surface was exposed to atomic hydrogen produced from a hot W-spiral filament operated at T=1800 K. Well known (β_1-H_2) monohydride surface species (and the higher hydrides β_2-H_2 and β_3-H_2) are readily produced by this technique.[16]

The H^+ ESDIAD pattern from a saturated monohydride (SiH) exposure (3 L, H_2) is shown in Fig. 5. Figure 5(a) shows the raw ESDIAD pattern observed from such an exposed surface with an incident electron beam energy of V_{e^-}= 500 eV. Again, as in the "clean" crystal surface H^+ pattern shown in Fig. 3(a), a pronounced depression in intensity is observed near the electron gun side of the ESDIAD analyzer. The background pattern for the exposed surface is shown in Fig. 5(b) and is similar to that of a "clean", prepared surface (see Fig. 3(b)). A pronounced depression in intensity of the background signal is also observed in the center of the pattern, as described earlier from the "clean", prepared Si(111) surface. We note that the yield of the background signal to that of the raw ESDIAD data is $(Y_{bkgnd}/(Y_{H^+}+Y_{bkgnd})=62\%)$. This indicates that the background pattern, which is unrelated to the Si-H bond directions because H^+ ions are completely retarded during the accumulation of the background pattern by the RFA grid potentials, is substantial and must therefore be properly accounted for in quantitative measurements. Indeed, the final processed data shown in Fig. 5(c) clearly indicates that a broad H^+ ion emission pattern centered on the normal to Si(111) is observed for this monohydride coverage.[16] It is also clear that a similar interpretation of the raw ESDIAD pattern (Fig. 5(a)) from a H-exposed surface would be impossible without proper background subtraction. These general conclusions were reached by Dresser, et al. in the ESDIAD of NH_3 adsorption on Ni(110).[7] In that work, a comparison of raw and background-subtracted H^+ ESDIAD data clearly shows the improved ESDIAD patterns attained through digital acquisition and background subtraction.

IV. Summary

We find that the background effects in ESDIAD measurements on silicon are significant and must be properly eliminated in the interpretation of the H^+ ESDIAD patterns. Background yields from "clean" and H-exposed Si(111) surfaces are large and can be >50% of the raw ESDIAD signal. The source of the background yield is due to soft x-ray emission from the silicon surface and/or the retarding field analyzer grid support rings. The background subtraction is of major importance for ESDIAD measurements made on adsorbates giving relatively low yields of desorbing ions.

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Figure Captions

Figure 1. Digital LEED/ESDIAD apparatus for silicon surface studies.

Figure 2. Dark current measurements of the ESDIAD apparatus (crystal rotated out of the electron beam). (a) x-y plates grounded, V_x=V_y=0 V; (b) V_x=56.4 V, V_y=0 V; (c) V_x=0 V, V_y=-6.6 V; (d) V_x=56.4 V, V_y=-6.6 V.

Figure 3. ESDIAD patterns obtained from a clean, prepared Si(111)-(7x7) surface (crystal biased at +100 V). Raw ESDIAD pattern; (b) Background pattern; (c) Processed (background subtracted) pattern. Crystal temperature is T=120 K.

Figure 4. Background yield as a function of: (a) incident electron kinetic energy and (b) electron current density. The observed linearity of the data suggests that a characteristic soft x-ray photon source, produced from electrons striking the Si(111) crystal, is primarily responsible for the observed background patterns.

Figure 5. ESDIAD patterns from a saturated monohydride (SiH) exposure (3L, H_2) of atomic hydrogen on Si(111)-(7x7). (a) Raw ESDIAD pattern from the exposed surface; (b) Background pattern; (c) Processed (background subtracted) pattern, where a broad, normally-oriented Si-H species is postulated. Crystal temperature is T=120 K during ESDIAD measurement.

Cross-sectional View of Digital LEED/ESDIAD Apparatus

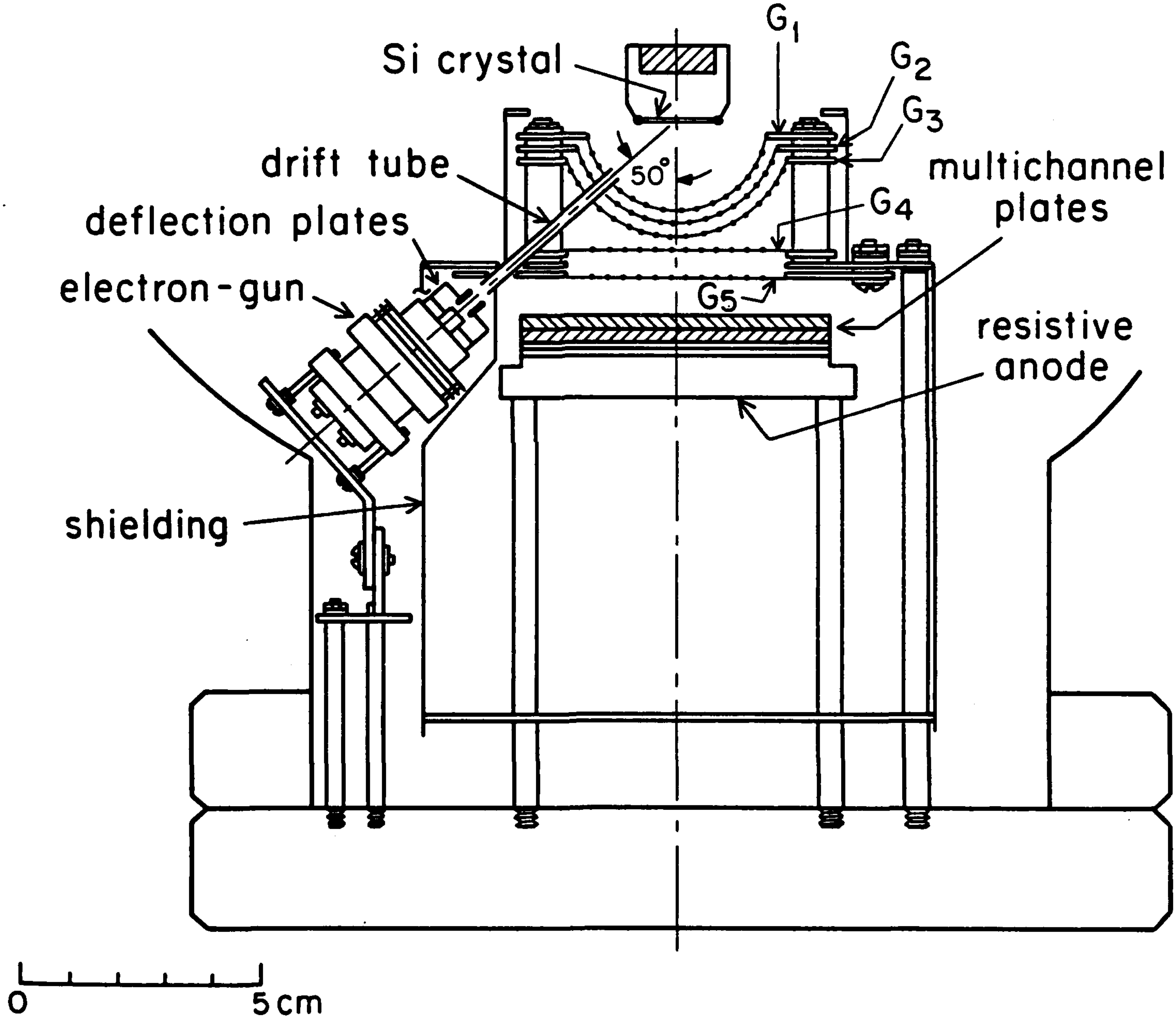

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Figure 1

Dark Current Patterns

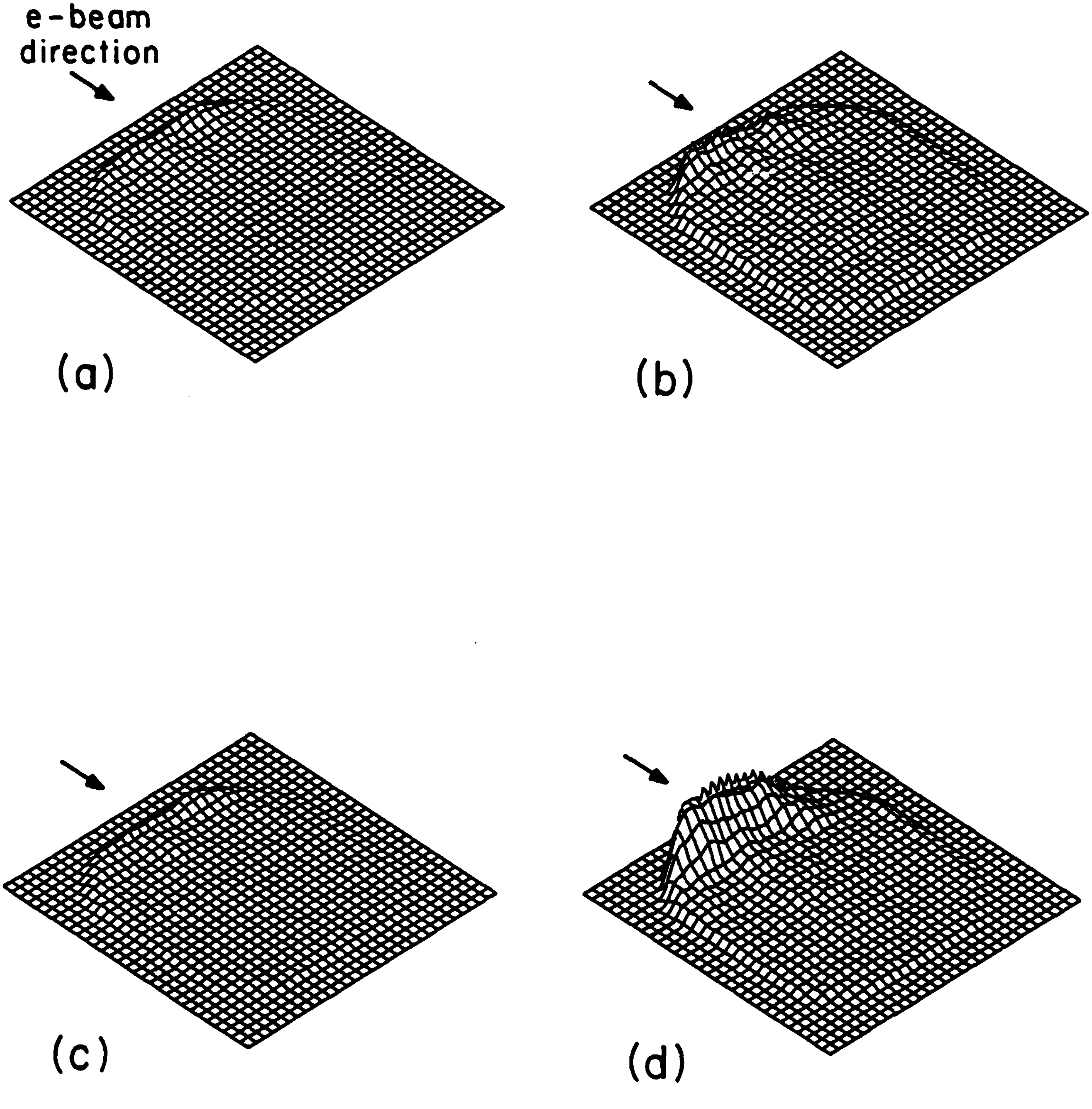

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Figure 2

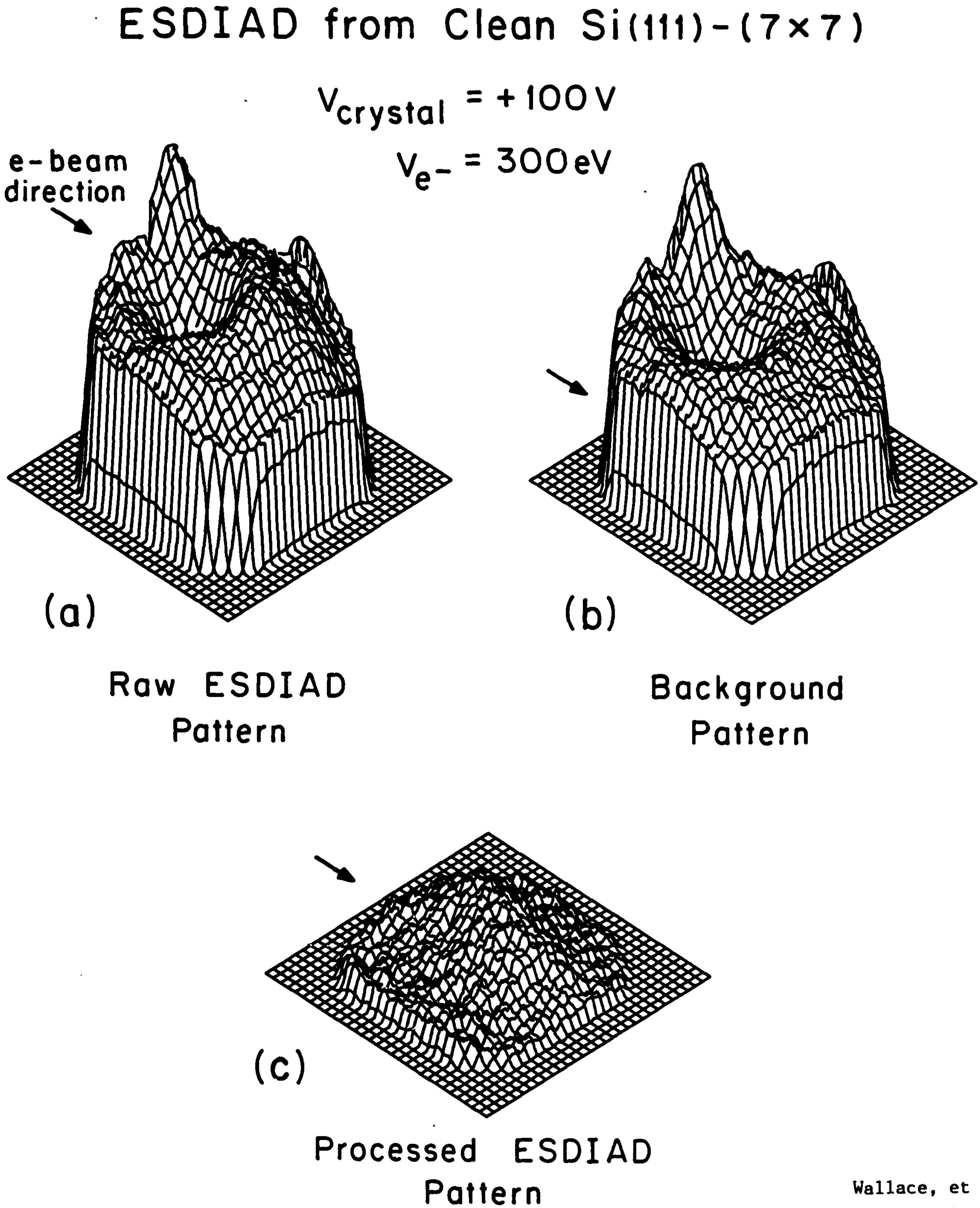

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Figure 3

Total Background count dependence on electron energy and current density

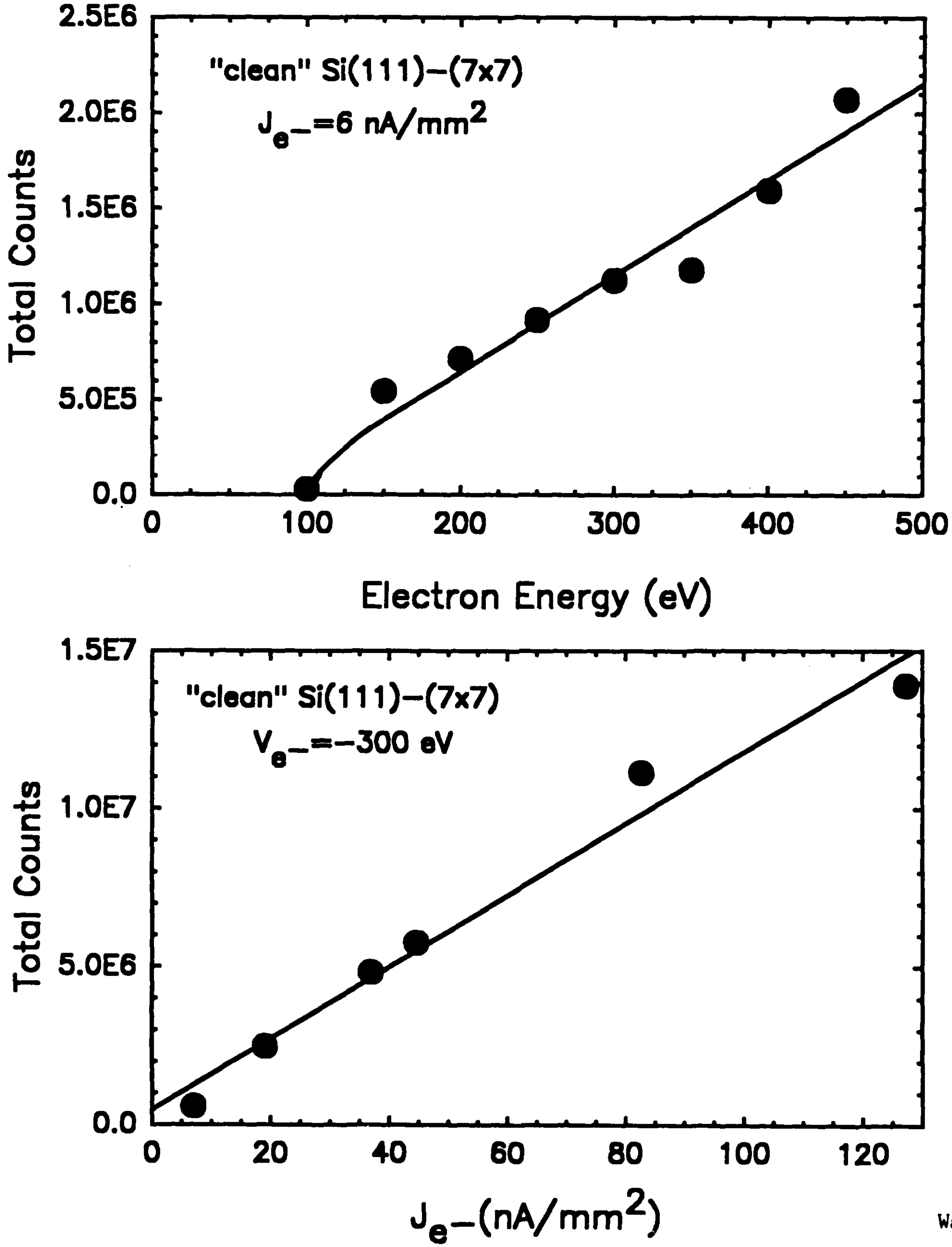

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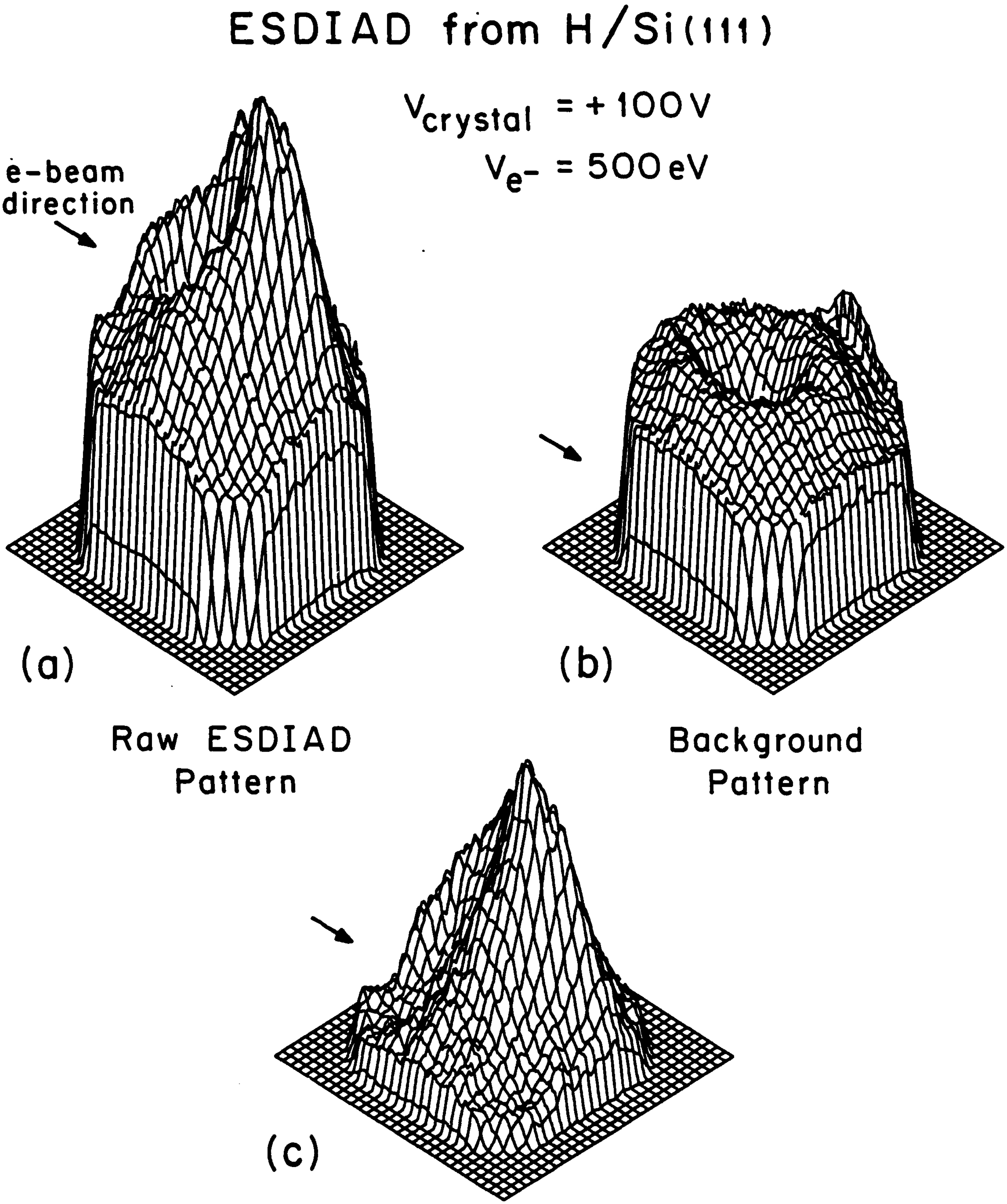
Figure 4



Raw ESDIAD Pattern

Background Pattern

Processed ESDIAD Pattern

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Figure 5

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