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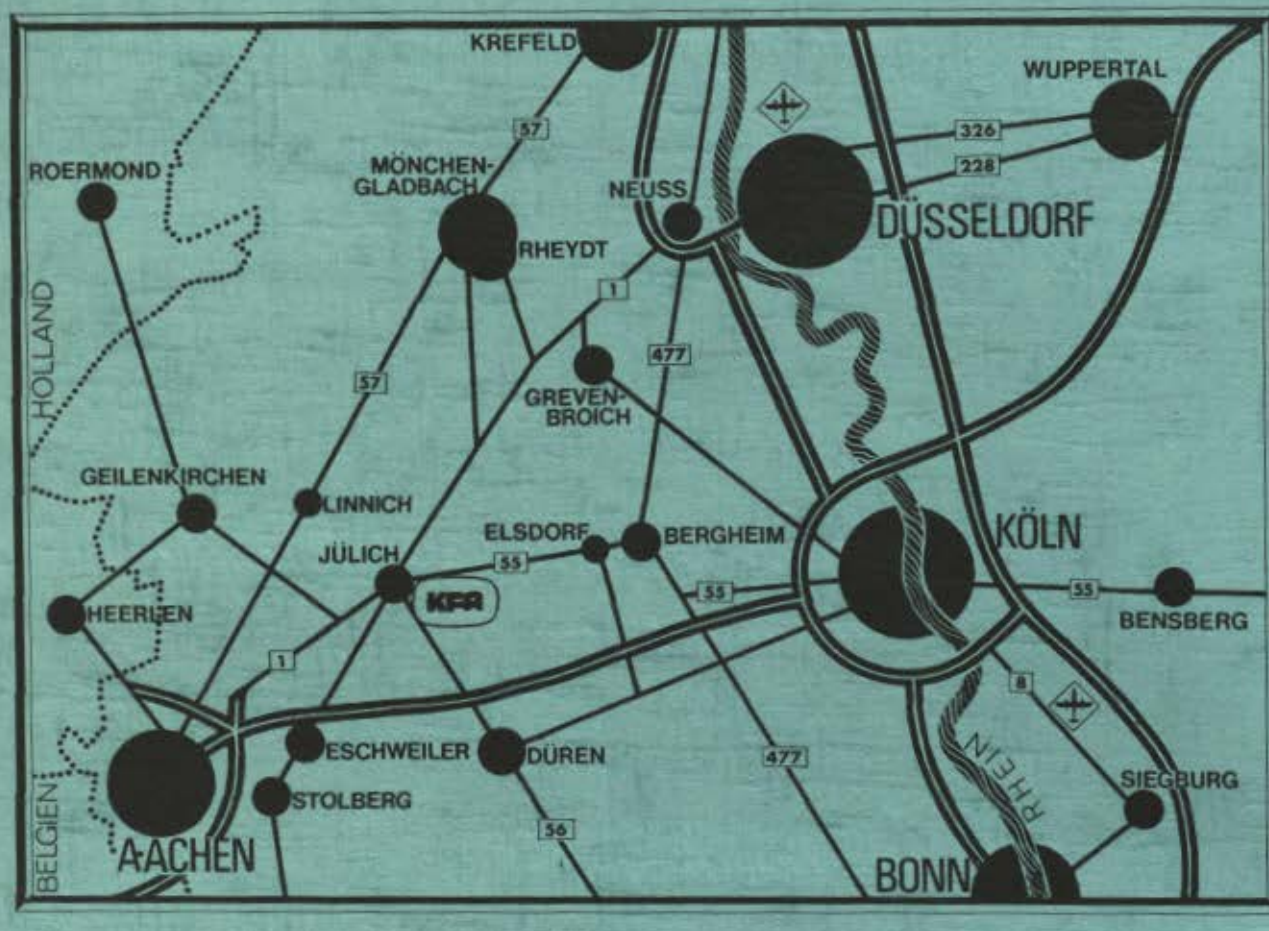

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SURFACE STATE TRANSITION AND SURFACE BAND STRUCTURE OF SILICON

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+) The experimental part of this work was performed at the 2. Physikalisches Institut and Sonderforschungsbereich Festkörperelektronik, Aachen.

Abstract

High-resolution energy loss spectroscopy has been studied with low-energy electrons scattered from clean silicon (111) surfaces. The spectra show losses due to transitions between occupied and empty "dangling bond" surface state bands. Two of such loss peaks centered around 0.54 and 2.25 eV are observed with surfaces exhibiting the metastable Si (111)-2x1 cleavage structure, while after the structural conversion to the stable 7x7 structure only one loss centered around 1.7 eV is found. These peaks indicate two and one saddle points , respectively, in the energy difference function $(E_1(\underline{k}) - E_2(k))$ of the "dangling bond" surface bands correlated with the 2x1 and the 7x7 silicon (111) surface structures.

A high density of surface states has been reported for silicon (111) surfaces in numerous papers [1]. The pinning of the Fermi-level on cleaved surfaces for n- and p-dopings has been described by two surfaces state bands, one below and one above the Fermi-level. Realistic calculations of the surface band structure are complicated since such surfaces are reconstructed. The cleaved surface exhibits a metastable (111)-2x1 structure which converts to the stable 7x7 structure upon annealing above 350 to 390^{o}C depending on the density of cleavage steps [2 - 4]. Correlated with the structural transition pronounced changes in the band bending and the electron affinity, i. e. in the surface state distribution and the surface dipole, respectively, have been observed [3, 4].

For unreconstructed surfaces theoretical studies have revealed that the above discussed surface states are an intrinsic property of two-dimensional flat surfaces and are caused by the "dangling bonds" of the silicon surface. In addition, deep lying surface states due to a surface relaxation have been found [5 - 7]. The splitting of the dangling bond surface band into two bands, one above and one below the Fermi-level, however, was not reproduced by these calculations and is probably related to the reconstruction. While the lower, occupied part of the dangling bond surface band has been observed in UPS [8 - 10] little is known about the unoccupied part above the Fermi-level. Only the lower band edge has been determined from the surface photoconductivity threshold [11].

In this paper we report on high-resolution electron energy loss spectra (ELS) for cleaved and for subsequently annealed silicon (111) surfaces. These spectra exhibit several losses due to surface state transitions. For the freshly cleaved surface two energy loss peaks centered around $\Delta E = 0.54$ eV and $\Delta E = 2.25$ eV, respectively, are attributed to transitions between the occupied and the empty "dangling bond" surface band. The extremly strong peak at 0.54 eV is only observed with the cleaved surface and is thus related to the 2x1 surface reconstruction.

Single crystals of p-type silicon (4000 Ωcm) were oriented, cut into 15x6x6 mm^3 blocks and mounted on a cleavage tool in an ultrahigh vacuum chamber which had a base pressure of 5×10^{-11} Torr. Characteristic ELS-spectra were measured with a two axis spectrometer [12] for various primary energies and angles of incidence. In addition to Si, also ZnO [12], Ge, and GaAs were investigated[+]. For this class of materials the structure in the loss spectra is independent of the primary energy and does not depend on the angle of incidence, contrary to the findings on Ni [13, 14], where strong energy and angle dependent "loss" structures are observed. The results for Si are presented in Fig. 1-3. Compared to the studies with a cylindrical mirror analyser [7] the loss spectrum itself rather than its second-derivative already reveals sharp structures (Fig. 1). This is due to the higher resolution in energy and in angle

[+] The results on Ge and GaAs will be published elsewhere.

of the spectrometer used here. Since only those energy losses are observed where the momentum transfer parallel to the surface is small a broadening of the peaks caused by dispersion effects is avoided.

At the freshly cleaved silicon surface exhibiting the Si (111)-2x1 structure five pronounced loss peaks are observed for energies less than 10 eV (Fig. 1). While the energy losses E_1 and E_2 are both due to bulk interband transitions the peaks labeled S_0, S_1, and S_2 are caused by transitions involving surface states. The different nature of the observed losses can be shown in several ways. On the one hand, the peaks S_0, S_1, and S_2 are strongly sensitive to surface treatments. They are observed to disappear after oxygen adsorption (see also ref. 7) and to disappear and to change in energetic position, respectively, if the 2x1 cleavage structure is converted to the stable Si (111)-7x7 structure (see Fig. 3). On the other hand, the experimentally observed loss spectrum may be compared to a calculated one based on bulk optical data. It has been shown [12, 15] that energy losses even at low electron energies are described by the dielectric scattering model. According to this model the intensity of the energy losses is proportional to the loss function - Im $(^1/_{(\varepsilon + 1)})$ corrected by a factor strongly depending on the loss energy. This correction accounts for the varying part of the electrons inelastically scattered into that window in k-space which is accepted

by the analyser [12]. The dashed curve in Fig. 1 gives the corrected loss function calculated from the bulk dielectric constant ε [16]. It is evident that the losses S_0, S_1, and S_2 are not described by the bulk data and thus are due to transitions involving surface states. In the following only the loss peaks S_0 and S_1 shall be considered. The peak S_2 and another one, S_3, at 14.5 eV have been already attributed to transitions involving the surface bands correlated with the back bonds of the relaxed surface [5, 7].

The most prominent feature in the loss spectra of the freshly cleaved surface is S_0 which corresponds to a strong optical absorption in the surface layer. Chiarotti et al. [17] have reported absorption spectra after multiple internal reflection for clean and for subsequently oxygen covered, cleaved silicon surfaces. The difference between the absorption of both surfaces is replotted in Fig. 2 together with the energy loss spectrum. Obviously, the same absorption band is observed in both experiments. While, however, in IR-absorption the band has been extracted from the data after a procedure that not necessarily reveals the true properties of the clean surface the absorption band can be observed directly in ELS. The minor deviations in shape and in peak position are caused by the different experimental methods.

The absorption band S_0 has been attributed [17] to transitions between two bands $E_1(\underline{k})$ and $E_2(\underline{k})$ of surface states around the

Fermi-level. The peak itself is then due to a saddle point in the energy difference function $(E_1(\underline{k}) - E_2(\underline{k})) = E_{12}(\underline{k})$ since such a critical point of a two-dimensional band structure exhibits a logarithmic singularity in the joint density of states [18]. A threshold at the low-energy side of the band gives the energy of the surface band gap. The extrapolation of the measured energy loss spectra to zero intensity yields 0.25 eV for the onset energy of the S_0 peak in excellent agreement with the value of 0.26 eV obtained by Chiarotti et al. from their optical measurements.

Photoelectric emission from occupied surface states below the Fermi-level has been observed with cleaved silicon surfaces [8 - 10]. As in other experiments [11, 17], the surface contribution has been evaluated as the difference between the photoemission energy distributions of the clean and of the subsequently oxygen covered, cleaved surface. For moderately doped silicon, the emission from surface states shows a band of about 1.8 eV full width which exhibits a maximum at 0.9 eV below the Fermi-level and has a tail up to this energy. This emission band is assumed to measure the density of states in the lower, occupied surface state band below the Fermi-level.

If the empty and the occupied surface state bands would be symmetrically arranged around the Fermi-level then the joint density of states and thus also the imaginary part ε_2 of the dielectric constant should exhibit a maximum at 1.8 eV. This energy compares with the S_1 peak at 2.25 eV in the energy loss spectrum of the cleaved

silicon surface. Therefore, it seems to be likely that the loss peak S_1 is to be explained by a maximum in the joint density of surface states as expected for symmetric surface state bands. However, the additional peak S_0 observed by optical as well as by energy loss spectroscopy indicates that the surface state bands are only partly symmetric.

Due to the lack of a scattering theory the number of surface states contributing to S_0 and S_1, respectively, cannot be evaluated. A rough estimate would give that only 10 to 20% of the total density of surface states contribute to the peak S_0.

The sensitivity of the surface transitions to the surface structure is demonstrated in Fig. 3. Correlated with the conversion of the 2x1 superlattice into a 7x7 structure the S_0 peak disappears and the S_1 peak at $\Delta E = 2.25$ eV shifts to a lower energy $\Delta E = 1.7$ eV. The bulk transitions E_1 and E_2 slightly change their positions on the energy scale as well. This is not surprising since at these low primary energies ELS measures the optical properties of the sample very close to the surface.

Meyer [19] has reported ellipsometric measurements in the spectral range from 0.69 to 3.4 eV with clean and with oxygen covered silicon surfaces. From the difference between the signals measured with both surfaces he calculated the surface optical constants. In

addition to Si (111) surfaces exhibiting the 2x1 and the 7x7 structures, respectively, he also used Si (110) and (100) surfaces. For all four silicon surfaces he obtained an extra band about 1 eV wide and centered at 2.6 eV. However, contrary to Meyer's conclusion this band cannot be identified with the S_1 peak of ELS since, for example, this peak was observed to shift by 0.5 eV from 2.25 to 1.7 eV due to the structural conversion of the cleaved (111) surface. The structure in the spectral dependence of the optical constants deduced from the ellipsometric measurements might mainly be caused by a modulation of these quantities due to the electric fields in the surface space charge layer [20].

The results may be summarized as follows. The theoretical calculations give one "dangling bond" surface state band for the unreconstructed Si (111)-1x1 surface, which is half-filled [5, 6]. Due to the 2x1 reconstruction found with freshly cleaved Si (111) surfaces this single band splits into two bands. The energy gap between these bands has been determined to be 0.25 eV. The lower edge of the upper band is located outside the center of the surface Brillouin zone [11]. The bands are about 1.8 eV wide and partly symmetric. The energy difference function $E_1(\underline{k}) - E_2(\underline{k})$ of these two surface bands has two saddle points S_0 and S_1 at about 0.5 eV and 2 eV, respectively. After the conversion of the 2x1 cleavage structure to the stable 7x7 surface structure the 1st Brillouin zone is again reduced causing further splittings and probably also overlaps in the new surface band structure.

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Figure Captions

Fig. 1 ELS spectrum of a cleaved (111) silicon surface in specular reflection. E_1 and E_2 are bulk interband transitions. S_0, S_1, and S_2 are transitions involving surface states.

Fig. 2 Comparison of ELS spectrum and optical absorption [17] (dashed curve) for freshly cleaved Si (111)-surfaces.

Fig. 3 ELS spectra for a silicon (111)-surface after cleavage and after a subsequent anneal at 700°C in ultrahigh-vacuum.

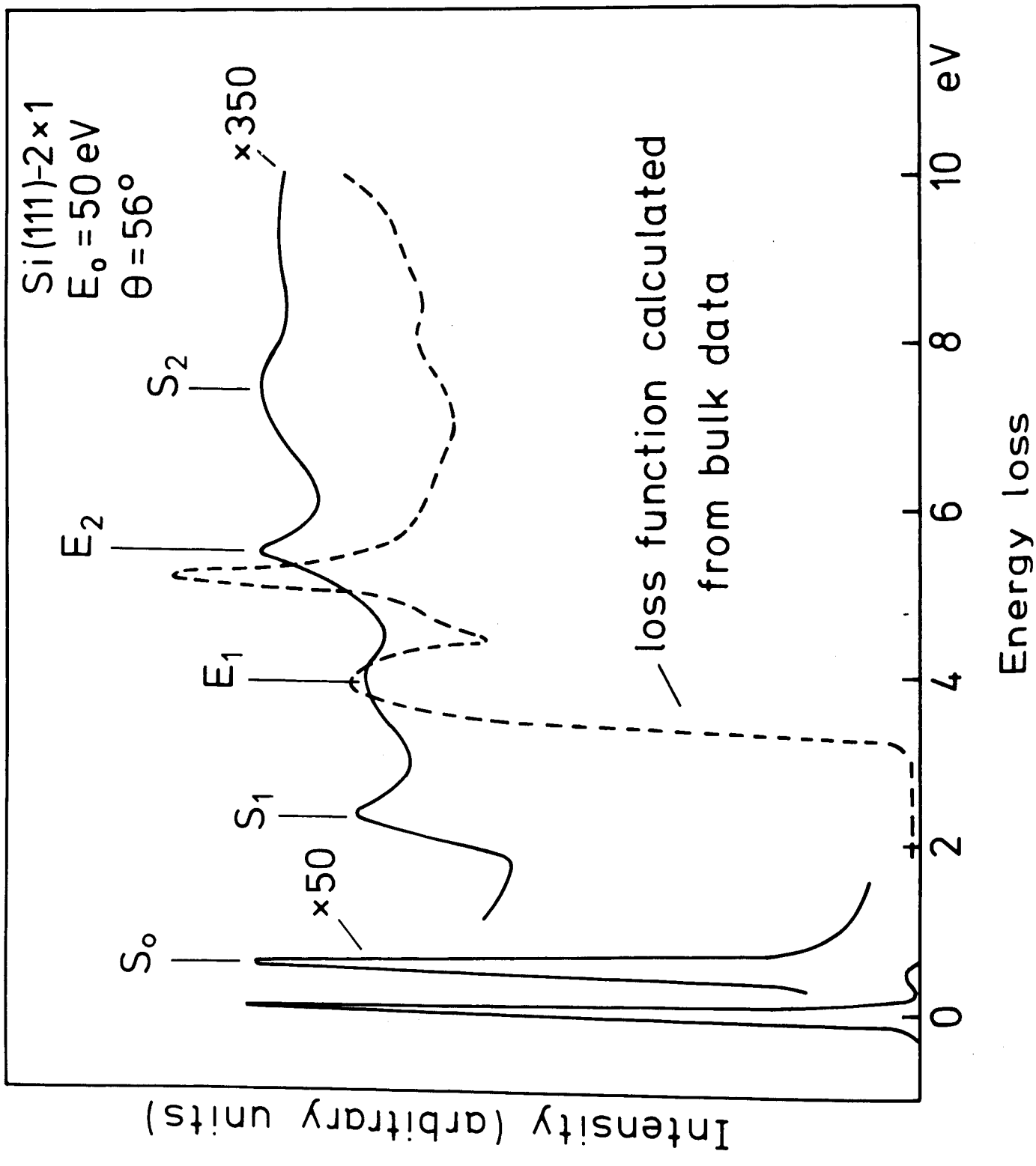
Si(111)-2×1
E₀=50 eV
θ=56°
×350
S₂
E₂
E₁
S₁
×50
S₀
loss function calculated
from bulk data
0
2
4
6
8
10 eV
Energy loss
Intensity (arbitrary units)

Fig. 1

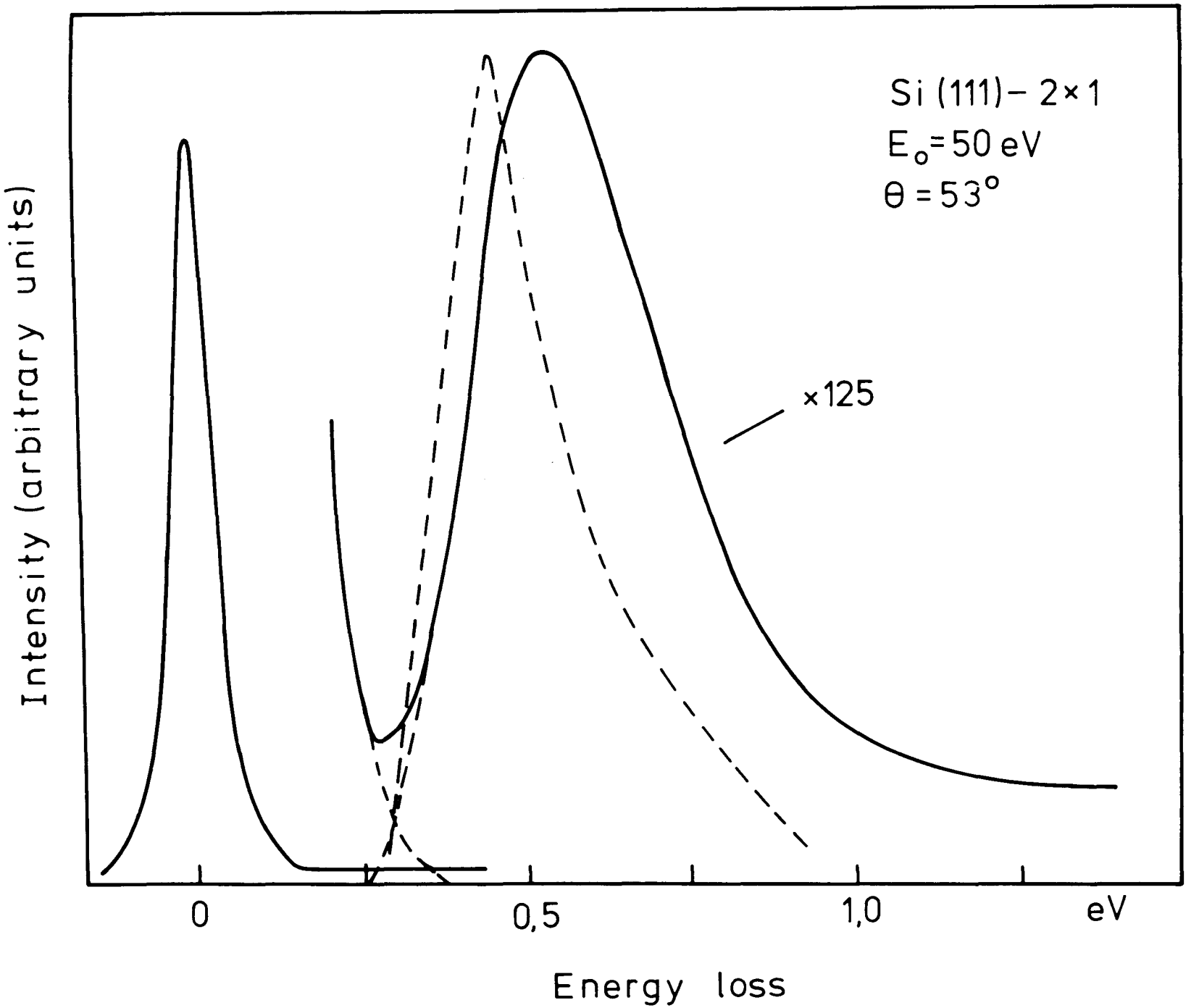
Si (111)– 2×1
E_o=50 eV
θ = 53°
×125
Intensity (arbitrary units)
0
0,5
1,0
eV
Energy loss

Fig. 2

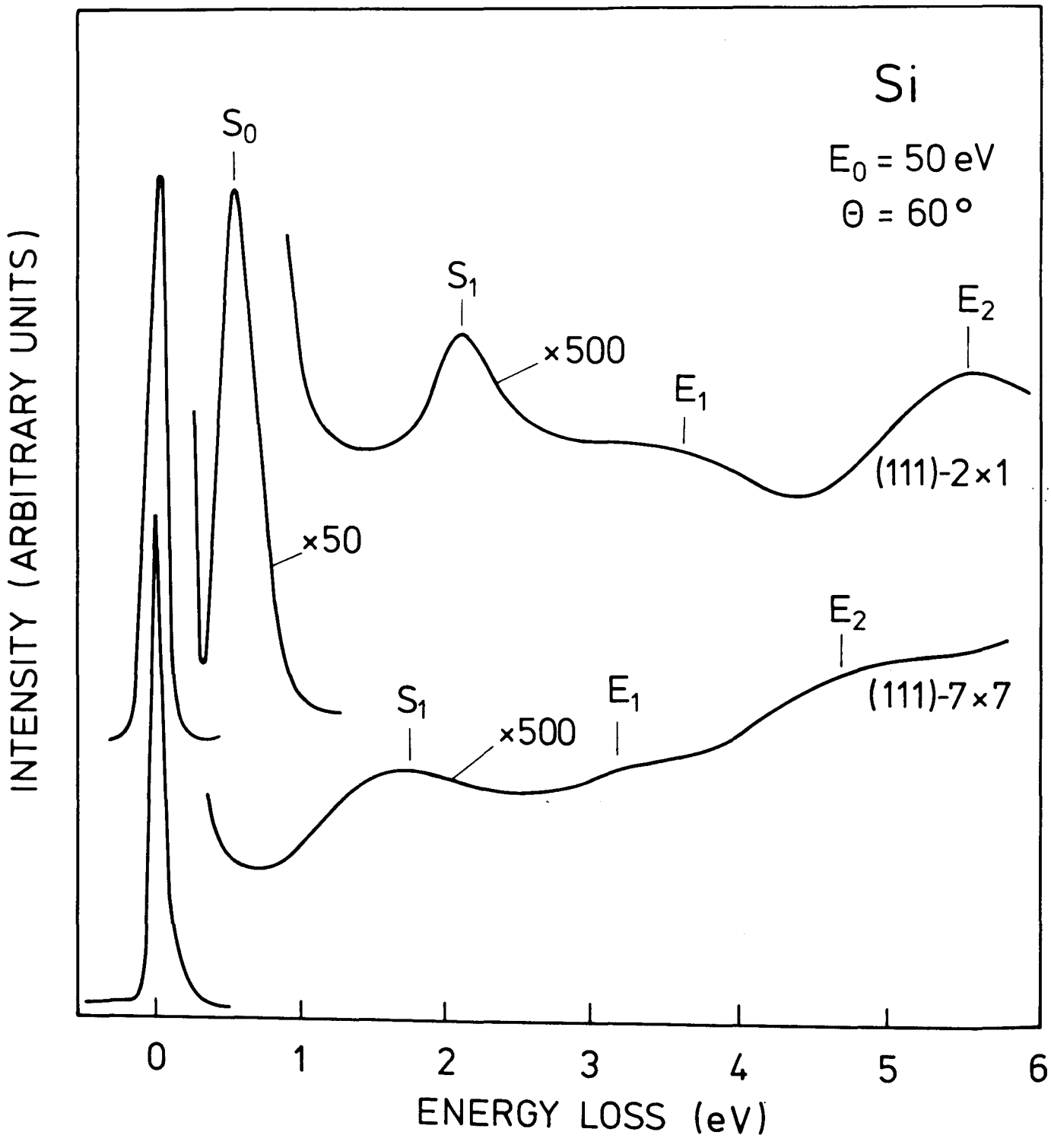
Si
E_0 = 50 eV
Θ = 60°
S_0
S_1
E_1
E_2
×500
×50
(111)-2×1
(111)-7×7
INTENSITY (ARBITRARY UNITS)
0
1
2
3
4
5
6
ENERGY LOSS (eV)

Fig. 3

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