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Abstract

The structure of the germanium-silicon interface has been analyzed by x-ray standing waves in anultra-high vacuum environment. Structural models of the Si(111)7x7 surface have been tested through the structure and energetics of the Si(111)7x7-Ge interface. Our results agree with the dimer-adatom stacking-fault (DAS) model of Takayanagi et al. for the bare surface. At the interface Ge atoms occupy the atop sites on the surface atoms that offer dangling bonds as well as on the adatoms of the DAS model of the Si(111)7x7 surface.

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The fundamental and technological importance of the phenomena associated with interfaces has led to a rapid growth of interest in the studies of (quasi) two dimensional systems, such as solid-vacuum (surfaces), solid-gas, solid-liquid and solid-solid interfaces. The knowledge of interface atomic structures is of primary importance for an understanding of the associated properties. Upon creation of a crystal surface, the atoms in the interface region are often redistributed. For example, on a silicon (111) surface, prepared by sputtering and annealing in ultra high vacuum (UHV) environment, the atoms are rearranged in such a way that the lattice periodicity parallel to the surface is 7 times enlarged compared to the ideal surface. The actual atomic arrangement in this 7x7 superlattice structure on Si(111) surface is not yet fully determined, although it has been the subject of many investigations for almost three decades.

A great deal of progress has been made over the past few years in the development of techniques to measure surface and interface structures with high local precision. Scanning tunneling microscopy (STM) has revealed the surface topology on the atomic scale,transmission electron microscopy (TEM) and diffraction (TED) have recently been advanced to give detailed information of the surface reconstruction. Ion scattering spectroscopy and surface extended x-ray absorption fine structure (SEXAFS) measurements were done to determine the atomic geometry of the surfaces. The kinematic x-ray scattering is attacking the surface structure problem in the same way as it has been used with tremendous success for the bulk structures. Finally, coherent x-ray interference was used in studies with x-ray standing waves (XSW) to determine the position of surface and adsorbed atoms relative to the substrate bulk diffraction planes. While the position accuracy of most of these techniques seems to be limited to about ≥ 0.1 Å, SEXAFS and XSW, which have profited tremendously by the availability of intense synchrotron radiation sources,

can give results even with a resolution better than 0.01 Å. Except SEXAFS all other techniques have been applied to the challenging silicon (111)7x7 surface and most to the Germanium-silicon interface as well. XSW results were reported for the relaxation of the 7x7 reconstructed surface[1] and for the Germanium-silicon interface[2]. Both studies have given different results in comparison to those from other methods and it is therefore of utmost importance to understand the reason for the discrepancies.

In a preliminary study we have already reported XSW measurements with quite different results from those in refs. 1 and 2 [3]. We have now reinforced our previous observations[3] with more measurements which we report here to complete the picture of the structure and give insight into the energetics of the overlayer growth. We will additionally show that, for XSW analysis on interfaces of complicated structure, it is of utmost importance to make measurements under UHV conditions, to do systematic studies with different adsorbate densities and preparation conditions, and to include different Fourier components of the density function in the analysis.

We have studied the geometrical structure of the Si(111)7x7 surface by forming a silicon-germanium interface through the adsorption of Ge. Because of the isoelectronic valence shell, and thus the chemical similarity, of Ge and Si the adsorption of Ge is not expected to perturb the silicon surface structure significantly. Moreover, the adsorption process itself is interesting. It is the primary stage in the epitaxial growth of thin films. The geometrical structures of surfaces and the way they change upon addition of a second material determines the electronic properties across the interface.

XSW has recently been successfully applied to determine the position of adsorbed atoms on crystal surfaces[4-6]. In this letter we report XSW measure-

ments on the Si(111)-Ge interface. The experiments were carried out at the wiggler beam line at the Hamburg Synchrotron Laboratory HASYLAB. The (111) surface of silicon samples was sputter cleaned with argon ion bombardment, annealed at 950°C, and characterized by low energy electron diffraction (LEED) and ultraviolet photoemission spectroscopy (UPS). A sharp 7x7 LEED pattern was observed. The cleanliness of the surface was checked by monitoring the silicon valence band and the germanium 3d line shape and intensity in the photoemission spectra. Germanium atoms were deposited on the clean Si(111)7x7 surface in a molecular beam epitaxy (MBE) apparatus. The surface retained the 7x7 LEED pattern in the presence of adsorbed germanium. The coverage of germanium was determined with a quartz oscillator as well as by comparing Ge fluorescence yield from the sample with that from a standard. Germanium was evaporated onto hot (530°C) substrates. During the in situ XSW measurements the pressure in the small transportable UHV chamber was maintained at 10^{-7} Pa or better. The XSW experimental set-up with the transportable UHV chamber at the wiggler beam line has been described in ref. 3.

By using the regular spatial peridicity of x-ray standing wave fields (XSW) one determines the phase (Φ) and amplitude (f) of the H-Fourier component of the adsorbate density function relative to the (hkl) bulk diffraction planes. Φ and f are closely related to the actual positions of the adsorbed atoms and the fraction of the total number of atoms at each adsorption site. The quantities Φ and f are obtained by a least-squares fit of the normalized fluorescence yield to the dynamical theory of x-ray diffraction.

The results of two measurements using a (111) reflection are shown in Fig. 1 [7]. These are explained in terms of the dimer adatom stacking-fault (DAS) model of Takayanagi et al. for the bare silicon (111)7x7 surface[8], the top view of which is shown in Fig. 2(a). The side view of a part of the Si(111)7x7

unit cell in this model is shown in Fig. 2(b). In the DAS model, the 7x7 unit cell is divided into two equal triangular halves, one of which has regular diamond structure stacking, whereas the other half has stacking-faults in the surface region. Region I shows the normal stacking sequence 123456, and region II shows the stacking-fault in the surface region: 56'. In the DAS model there are 12 Si adatoms (each bonded to 3 surface Si atoms) and 6 surface Si atoms (not bonded to any adatom), each of which provides a dangling bond for chemisorption. Our results are explained by adsorption of Ge atoms at the surface-atop [A, B in Fig. 2(b)] sites for low coverage and coadsorption at the surface-atop and the adatom-atop [C, D, E, F in Fig. 2(b)] sites for higher coverage, with a fraction of the Ge atoms in random distribution. When germanium atoms occupy only the surface-atop sites, the expected phase value from a (111) Bragg reflection XSW measurement is 0.89 d_{111}. Adsorption only at the adatom-atop sites would give rise to a phase value of 1.14 d_{111}. Occupation of sites of both types with equal population would give 1.02 d_{111}. The measured phases of 0.87$\pm$ 0.02 (Fig. 1, curve 1) and 1.06 $\pm$ 0.02 (Fig. 1, curve 2) for germanium coverages of 0.2 ML (monolayer) and 0.4 ML, respectively, are explained by assuming that at low coverage only surface-atop sites (position 0.89) are occupied, and with increasing coverage, the surface-atop sites having been filled, the only available adatom-atop sites (position 1.14) are occupied giving rise to an effective phase value between the two limits. In fact with the proper weight factor[9] - 6 surface-atop and 12 adatom-atop sites per 7x7 unit cell - the expected phase value is 1.07 d_{111}. The assumption of preferential filling on hot substrate is corroborated by the results of measurements on Si(111)-Ge interface using a (220) Bragg reflection.

The results of two measurements with a (220) reflection are shown in Fig. 3. In order to point out some important features with respect to (220) measurements, let us focus our attention on the atoms A and B at the surface-atop sites in region I and region II, respectively [Fig. 2(b)]. In XSW measurements the fluorescence response from an adsorbed atom depends on the distance of that atom from the nearest diffraction plane. Therefore, the atoms A and B ($d_{A_1} = d_{B_1}$) would give rise to the same fluorescence angular profile for (111) reflection measurement. However, due to the stacking-faults in region II, atoms A and B have different distance components ($d_A \neq d_B$) with respect to (220) planes. The expected fluorescence angular profile from the Ge atoms at site A[10] is shown by curve a ($d_A = 1.02\ d_{220}$), and the corresponding profile for site B is shown by curve b ($d_B = 0.69\ d_{220}$) in Fig. 3. The expected joint profile is the fitted curve 1 to the data corresponding to a phase value of (0.85 $\pm$ 0.02) d_{220} for 0.2 ML Ge coverage. The observed coherently adsorbed coverage of Ge atoms (0.2x0.60 or 0.12 ML) is what would be expected if only all the A and B sites, i.e. the surface-atop sites, are occupied. There are 6 such sites per 7x7 unit cell, while 49 corresponds to a monolayer.

The fluorescence response from a (220) measurement for a higher Ge coverage (0.5 ML) is shown by curve 2 in Fig. 3. This is explained as follows. Adsorption at C and D sites would give rise to similar response to that for adsorption at the B site [$d_C = d_D = d_B$, Fig. 2(b)]. The number of such sites per unit cell is 12. Therefore, occupation of all the available atop sites would give rise to a joint response close to the curve b. In fact, with proper weight[9] - 3 atoms at 1.02 d_{220} and 15 atoms at 0.69 d_{220}- the expected phase of 0.72 d_{220} agrees well with the observed phase of 0.75 $\pm$ 0.01 (curve 2 in Fig. 3). The fit corresponds to a coverage arising from the occupation of all the atop sites (0.37 ML).

The results of (111) and (220) reflection measurements, as described above,

For 0.2 ML Ge coverage clearly demonstrate the presence of stacking-fault only in one half of the Si(111)7x7 unit cell, and rule out the models involving stacking-faults in the entire region of the 7x7 unit cell. The results for higher Ge coverages show in addition to the presence of stacking-faults, the existence of adatoms in the unit cell. Thus, our XSW results agree only with the dimer adatom stacking-fault (DAS) model of the Si(111)7x7 surface by Takayanagi et al.[8].

The fact that Ge can be adsorbed preferentially at the surface-atop site for lower coverages indicates a higher binding energy for Ge at the surface-atop site compared to the adatom-atop site. Higher substrate temperature during Ge evaporation helps an adatom to diffuse on the surface before it settles in a deeper potential well.

Deposition of 0.4 ML Ge on substrate at room temperature maintained the 7x7 symmetry. XSW results showed the occupation of only surface-atop sites in contrast to the occupation of both surface-atop and adatom-atop sites for 530°C growth temperature. These results are comparable to the recent observation of the preservation of a 7x7 periodicity, and the proposed absence of the periodic array of adatoms at a buried amorphous-Si/Si(111) interface[11]. If the room temperature deposition of Ge removes the Si adatom from their regular position, the adsorption at the adatom-atop site is automatically ruled out.

For the adsorption at the one-fold atop sites, Ge contributing four electrons and Si one, the picture of bonding is not very clear. In fact, one may wonder whether the binding at the atop site is at all possible. A self-consistent field cluster calculation[12] involving one H atom and one Si atom, which is similar to a Ge atom attached to a single dangling bond of Si, however, suggests the possibility of binding.

In the present analysis a Si-Ge bond length of 2.40 Å, which is the average of Si-Si bond length in bulk silicon and the Ge-Ge bond length in bulk germanium, has been assumed. In the DAS model, the atomic displacements in the direction normal to the surface are not specified. We have assumed the bulk bilayer separation, 0.78 Å, for the distance between the adatom silicon and the suface silicon layer. This is within the error bar of the STM observation of 0.7 ± 0.1 Å [13].

Our results do not agree with the large contraction (0.5 Å) of the Si(111)7x7 surface recently measured by Durbin et al.[1], unless this relaxation is removed by Ge deposition. Because of the chemical similarity of germanium and silicon, and the unchanged 7x7 superstructure upon germanium deposition, the adsorption process is not expected to relieve a relaxation as large as 0.5 Å. Accommodation of this relaxation would require an unusually large Si-Ge bond length of 2.90 Å to explain our results. Note that the result of the (111) measurement for the 0.2 ML coverage, discussed without the knowledge of the results of our other systematic studies, could lead to a misinterpretation of this result, namely double layer growth[2] in connection with a (0.41 ± 0.06)Å inward relaxation of the substrate. This points up the need for coverage dependent XSW measurements with more than one Fourier component for complicated structures.

In most of our measurements we observe a fraction of germanium atoms that are not adsorbed at a particular site (random). Disorder was also observed for this system in previous channeling experiments[14].

Our results disagree with those of Patel et al.[2] who made open air XSW measurements on samples prepared in UHV and protected with amorphous silicon cap. A recent study on the interface between a silicon (111) substrate and amorphous

silicon has shown that the structure of the buried surface differs from that of the clean surface, even though the 7x7 periodicity is preserved[11].

In conclusion, the positions of the germanium atoms on silicon (111) surface have been determined by x-ray standing waves by measuring the distance components in the [111] and [220] directions. The structure of the bare silicon surface have been derived from the position of the adsorbed atoms, and has been found to support the dimer adatom stacking-fault model of Takayanagi et al.[8]. On this structure Ge atoms have been found to occupy the atop sites on the Si adatoms as well as on the surface atoms that offer dangling bonds. The present study shows that surface structures can be determined by tagging the surface atoms with chemically similar atoms. From the results of measurements made on samples prepared at different substrate temperatures it is concluded that the binding energy of germanium at the surface-atop site is higher compared to the adatom-atop site. The knowledge of energetics at the submonolayer level helps to understand the epitaxial growth process, which will be addressed in a later publication.

Acknowledgement

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7. Braggs law: $2d\sin\vartheta = \lambda$. In the present experiment a Bragg condition is selected for a particular value of λ (say, λ_B) and then scanning is performed in energy (i.e., λ) keeping ϑ fixed. The abscissae of Fig. 1 and Fig. 3 are $\Delta\lambda = \lambda - \lambda_B$. The equivalent $\Delta\Theta = \vartheta - \vartheta_B$ scales are shown at the top.
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10. The measurement showed that 40 % of the Ge atoms were randomly distributed. Therefore, the curves a and b have been calculated by assuming the remainder 60 % at either A or B sites respectively. The joint profile has been computed by assuming equal population - 30 % at A and 30 % at B sites.
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Figure Captions

Fig. 1 Measured (+) and calculated (---) reflectivity for silicon (111) reflection, R , and corresponding germanium K_α fluorescence yield, Y , as a function of wavelength of the incident x-rays. $\Delta\lambda(=\lambda-\lambda_B)$ is the deviation from λ_B that satisfies the Bragg condition. The range of $\Delta\lambda$ corresponds to an energy range of 3.6 eV. The equivalent $\Delta\vartheta(=\vartheta-\vartheta_B)$ scale is shown at the top. ●: Fluorescence data for a Ge coverage of 0.2 ML; □: Fluorescence data for a coverage of 0.4 ML.

Fig. 2 (a) Top view of the dimer adatom stacking-fault model of Takayanagi et al. showing the positions of the adatoms and the surface atoms that offer dangling bonds for chemisorption. The 7x7 unit cell is shown by the dashed lines. The dash-dot line divides the unit cell into two triangular subunits.
(b) Side view showing a part of the unit cell. Region I has normal diamond structure stacking (123456), and region II shows the stacking-faults in the topmost bilayer (56'). Ge atoms are shown at the surface-atop (A,B) and the adatom-atop (C,D,E,F) sites.

Fig. 3 Measured (+) and calculated (-·-) reflectivity for Si(220) reflection, R , and corresponding Ge K_α fluorescence yield, Y , as a function of $\Delta\lambda$. The range of $\Delta\lambda$ corresponds to an energy range of 1.1 eV. ●: Fluorescence data for a germanium coverage of 0.2 ML. □: Fluorescence data for a coverage of 0.5 ML. Curves a and b are those expected from the atom at A and at B [Fig. 2(b)] respectively. The effective response due to the occupation of both A and B sites is given by the fitted curve 1. Curve 2 corresponds to occupation of both surface-atop (A,B) and the adatom-atop (C,D,E,F) sites.

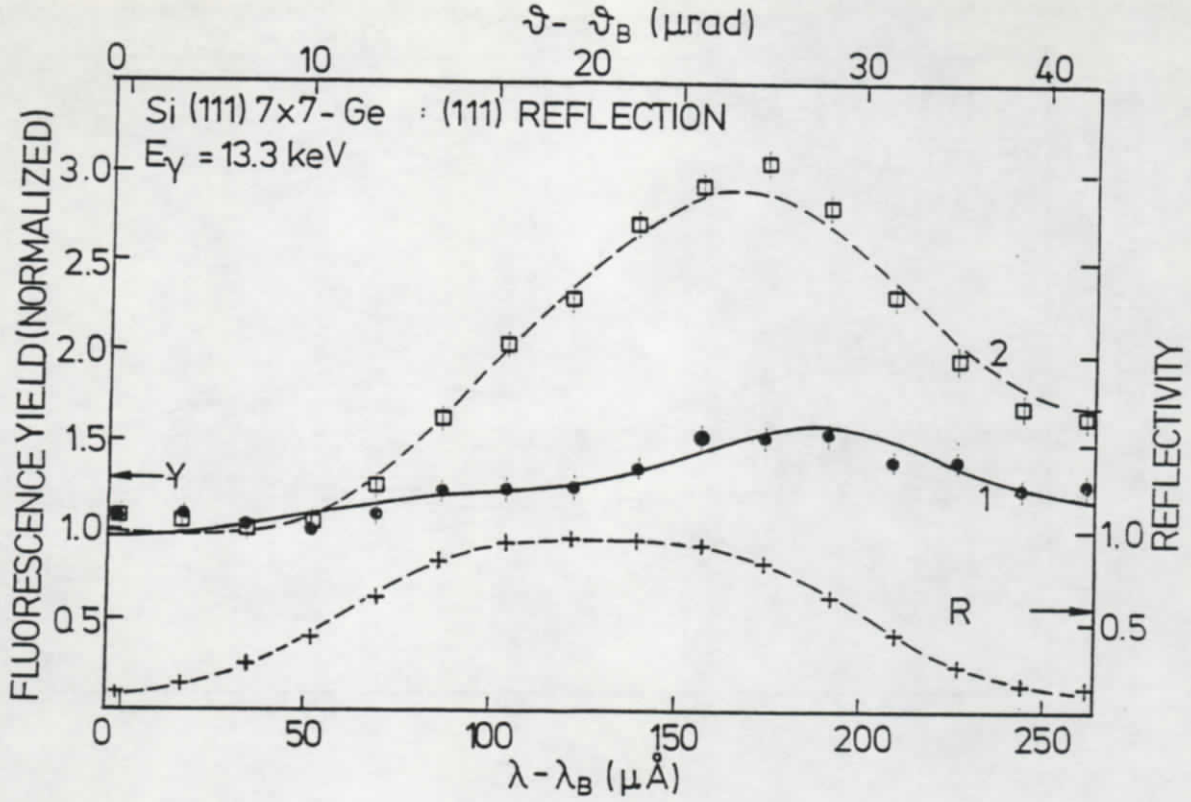
ϑ- ϑB (μrad)
0
10
20
30
40
Si (111) 7x7- Ge : (111) REFLECTION
EY = 13.3 keV
FLUORESCENCE YIELD (NORMALIZED)
3.0
2.5
2.0
1.5
1.0
0.5
Y
2
1
R
1.0
0.5
REFLECTIVITY
0
50
100
150
200
250
λ-λB (μÅ)

FIG. 1

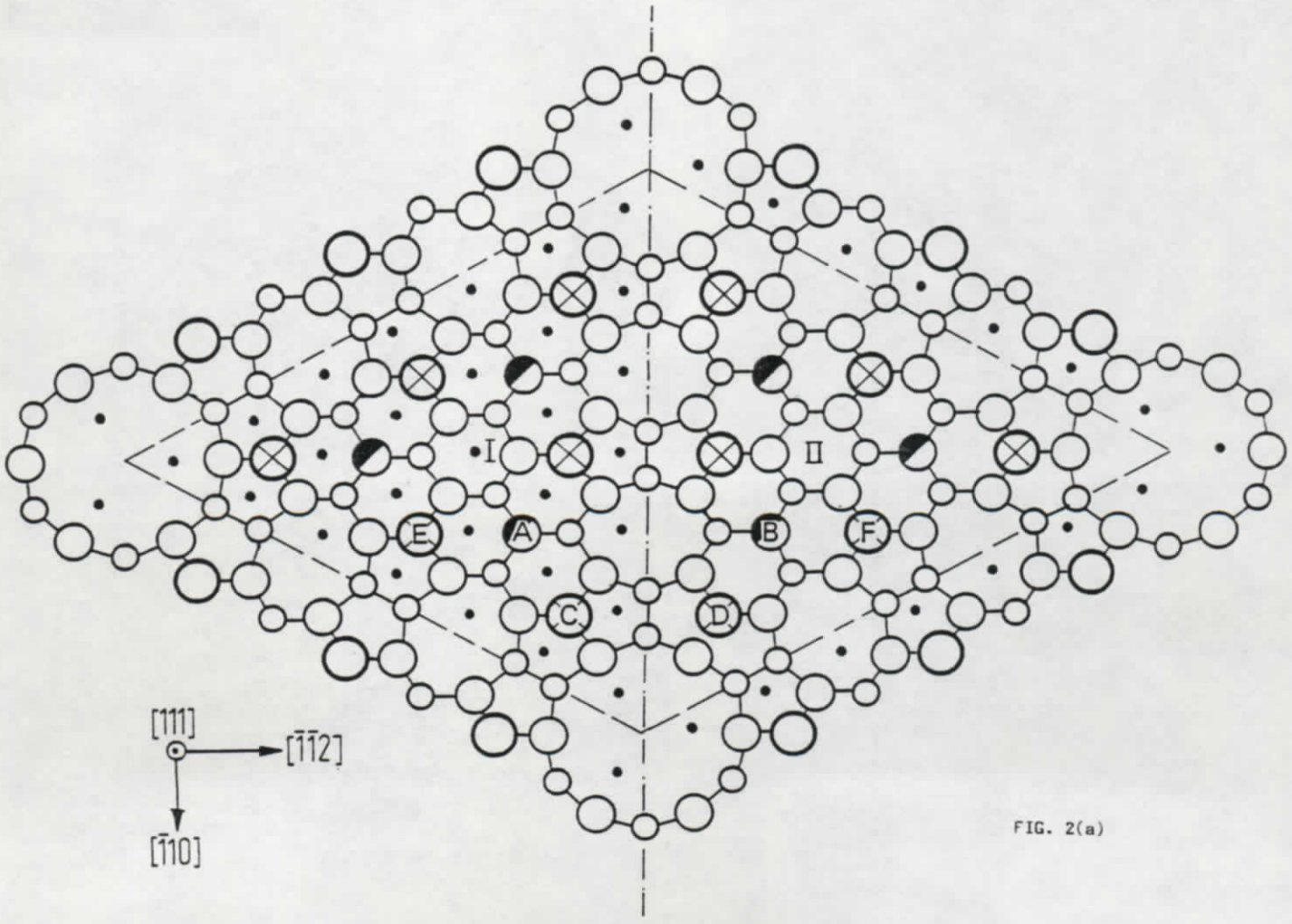
I
II
E
A
B
F
C
D
[111]
[$\bar{1}\bar{1}$2]
[$\bar{1}$10]

FIG. 2(a)

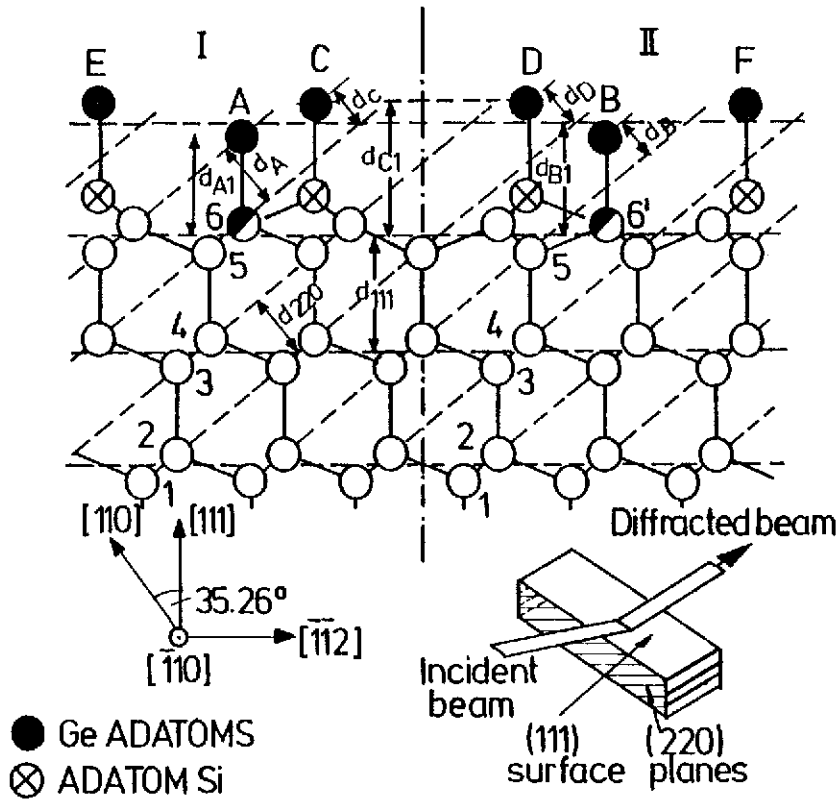
E
I
C
D
II
F
A
B
dA
dB
dC
dA1
dB1
dC1
6
6'
5
4
3
2
1
d220
d111
[110]
[111]
35.26°
[112]
[1̄10]
Diffracted beam
Incident beam
(111) surface
(220) planes
Ge ADATOMS
ADATOM Si
Surface Si not bonded to ADATOM Si
dA1 = dB1 = 0.89 d111 , dC1 = 1.14 d111 , d111 = 3.14 Å
dA = 1.02 d220 , dB = dC = dD = 0.69 d220 , d220 = 1.92 Å

FIG. 2(b)

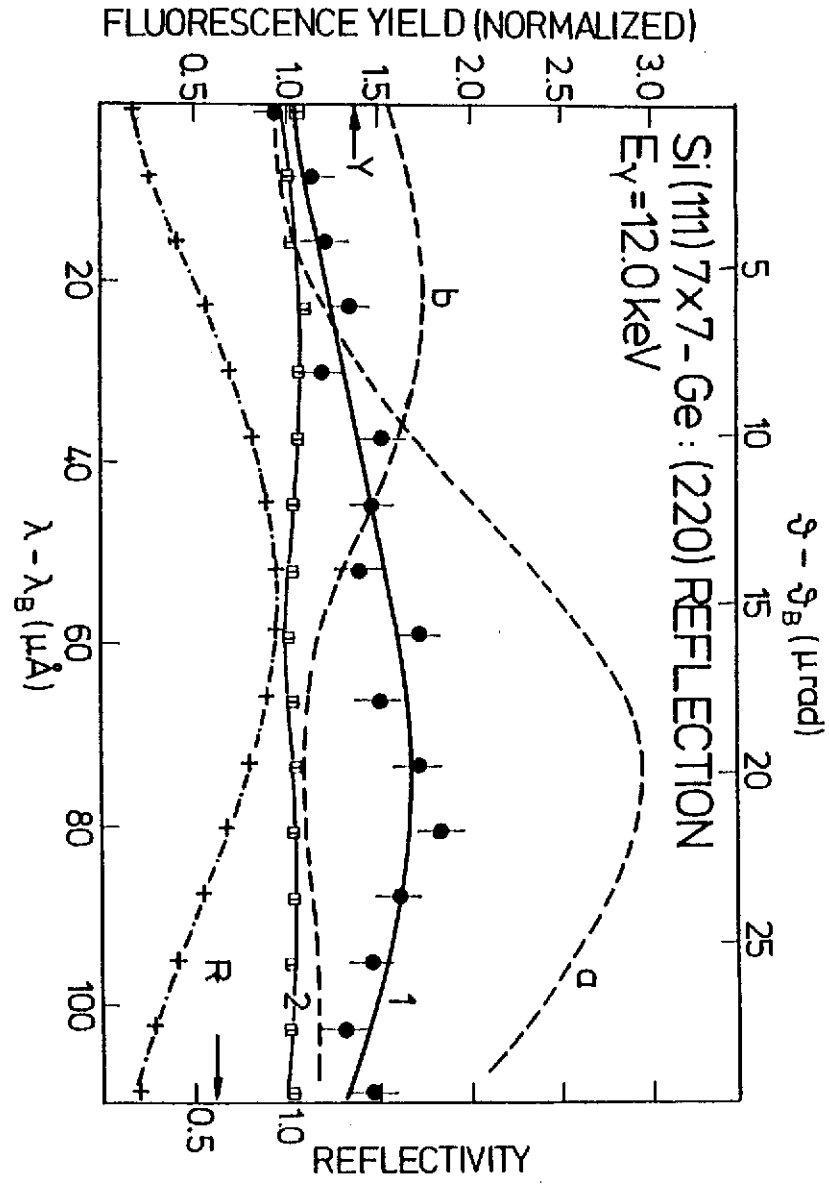
FLUORESCENCE YIELD (NORMALIZED)
Si(111) 7×7 - Ge : (220) REFLECTION
Eγ = 12.0 keV
λ - λB (μÅ)
ϑ - ϑB (μrad)
REFLECTIVITY
R
Y
a
b
1
2

FIG. 3