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Effect of dimensions on the vibrational frequencies of thin slabs of silicon

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Calculated frequencies of the long-wavelength vibrations of thin slabs of silicon parallel to the (111) plane show that the in-plane modes decrease almost exponentially in frequency with decreasing thickness of the slab. The out-of-plane modes have frequencies lower than the in-plane modes and decrease in the same fashion as the slab becomes thinner. This result is consistent with the observation that the Raman-active mode shifts toward lower frequencies in laser-annealed, ion-implanted silicon when the recrystallization is not perfect.

I. INTRODUCTION

In recent years growing interest has developed in materials that are not infinite crystals. Polycrystalline semiconductor heterostructures and materials have given rise to a great deal of fundamental work related to some of their exceptional properties. Amorphous and polycrystalline states are successive steps in the recrystallization process of ion-implanted materials when specific doping is intended for some particular use.

To account for the observation[1] that in laser-annealed ion-implanted silicon, depending on the degree of recrystallization, the Raman-active mode shifts from 520 cm^{-1}, the frequency of the Γ-point optical mode in a perfect crystal, to 516 cm^{-1}, we attempt to attribute this shift to the effect of dimensions on the vibrational properties in small crystallites of imperfectly recrystallized silicon.

It is now well established that real crystals, when their dimensions are relatively small, show, in addition to the normal modes of the infinite lattice, surface modes and effects of dimension; when the dimensions become extremely small only the surface modes persist.

In ionic crystals of finite thickness,[2] one finds two classes of modes: Those of the oscillatory spatial dependence and frequencies equal to the normal transverse- (TO) and longitudinal-optical (LO) frequencies at $\vec{q}=0$, in an infinite crystal, and those with an exponential dependence on distance across the slab and frequencies between ω_{LO} and ω_{TO}. More recent calculations[3] of the long-wave optical vibrational modes in finite ionic crystals of arbitrary shape have led to the same conclusions: In finite specimens there exist transverse and longitudinal bulk modes as well as surface modes which are neither transverse nor longitudinal and which have intermediate frequencies.

When the expansion of the displacement in plane waves is not used in the calculation of the vibrational frequencies of finite one-dimensional lattices,[4] one shows that the free ends produce "surface" modes of vibrations with frequencies in the forbidden gap between the optical and acoustical branches.

Surface modes and size effects have been calculated for many different systems. In a semi-infinite lattice[5] with the harmonic approximation, the normal modes are classified into "bulk" and "surface" modes. The surface modes exhibit an exponential decay of their amplitude away from the free surface because they have a complex wave-vector component normal to the surface. The frequencies of these modes lie in intervals which have, at most, their end points in common with intervals where bulk modes occur at the same transverse wave vectors.

Calculations for the surface mode in diamond and zinc-blende lattices[6] have shown that the details of the modes depend strongly on the structure of the surface: A very detailed knowledge of the geometric surface structure is necessary to make definite statements on frequencies of surface modes.

Our purpose here is to account for the variation of normal-mode frequencies with dimensions in a polycrystalline structure. A detailed calculation is impossible at present because of the poor knowledge of the exact structure of the interfaces. Therefore we believe that at this stage a useful exercise would be to give the general features of the observed correlation between the frequency shift of the Raman-active mode and crystallite dimensions on the basis of a very simple model.

II. THEORETICAL MODEL

For the purpose of examining the effect of the finite size of a homopolar crystal on the frequencies of the vibrational modes, we consider the simplest case, e.g., the case of a thin slab

extended to infinity in two directions. The slab is considered to consist of a number of layers, each of which has the thickness of a unit cell. In such a structure, the periodicity of the lattice is conserved along the two directions, and, consequently, the atomic displacements parallel to these directions can be expanded in plane waves, and the periodic boundary condition can be applied. Along the third direction neither of the above considerations is possible, and the sequence of cells along that direction is treated merely as one unit cell. As a result, the number of independent interactions increases considerably, for we have to account for interactions between plane lattices rather than three-dimensional ones. In fact, for a slab consisting of N unit-cell layers with n atoms per unit cell, the dynamical matrix needed to provide the vibrational frequencies is of $3nN\times 3nN$ dimensions. Associated with the above structure is a two-dimensional reciprocal lattice which displays a symmetry depending upon the orientation of the slab in the three-dimensional lattice. The corresponding two-dimensional Brillouin zone is a section of the three-dimensional one. Some reduction of the above-mentioned dynamical matrix for special points of the Brillouin zone may be possible if the orientation of the slab is chosen to be across directions of the crystal of high symmetry.

For the fcc lattice in which the group IV elements (Fig. 1) crystallize, the (111) plane is favorable, for it displays a relatively high symmetry and, moreover, the plane lattices parallel to that plane are described by two of the three unit vectors of the three-dimensional lattice. A new coordinate system $Ox'y'z'$ chosen so that the Ox', Oy' axes are coplanar with the slab while the Oz' direction is perpendicular to it, e.g.,

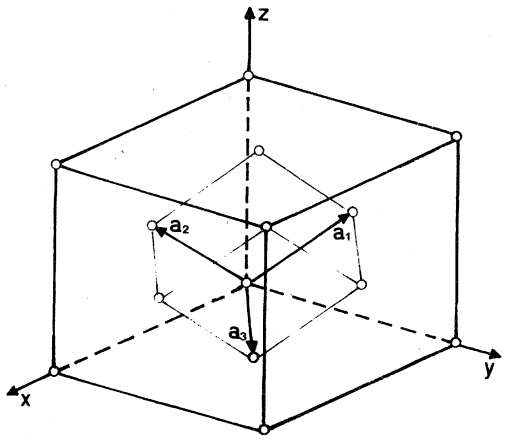

FIG. 1. Schematic representation of the face-centered-cubic lattice.

$$\vec{x}_0'=\frac{\vec{a}_1-\vec{a}_2}{|\vec{a}_1-\vec{a}_2|},\quad \vec{y}_0'=\frac{\vec{a}_1+\vec{a}_2}{|\vec{a}_1+\vec{a}_2|},\quad \vec{z}_0'=\frac{\vec{a}_1\times\vec{a}_2}{|\vec{a}_1\times\vec{a}_2|}, \tag{1}$$

where $\vec{a}_1,\vec{a}_2$ are the primitive lattice vectors.

The new coordinates of the atoms are given by the relations

$$\begin{pmatrix}x'\\y'\\z'\end{pmatrix}=H\begin{pmatrix}x\\y\\z\end{pmatrix}, \tag{2}$$

where H is the transformation matrix

$$H=6^{-1/2}\begin{pmatrix}-3^{1/2} & 3^{1/2} & 0\\ 1 & 1 & 2\\ 2^{1/2} & 2^{1/2} & -2^{1/2}\end{pmatrix}. \tag{3}$$

If the space group G of the original (three-dimensional) structure is symmorphic a similar transformation of the form

$$R_i'=HR_iH^{-1} \tag{4}$$

provides the new representations R_i' of the group elements. If the initial space group is nonsymmorphic, the associated translation vector $\vec{v}$ has to be transformed accordingly:

$$\vec{v}'=H\vec{v}\,.$$

Among the rotations in the new representation R_i' we choose only those which are associated with a translation $\vec{v}'$ whose z component is zero (if any), and which have the form

$$R_i'=\begin{pmatrix} & & 0\\ & S_i & 0\\ 0 & 0 & 1\end{pmatrix}, \tag{5}$$

where S_i is a 2×2 matrix.

The group G' of the so chosen elements is the "space" group of the new two-dimensional structure (slab) and can be used to provide the form of the force-constant matrices and the relations between the elements of the dynamical matrix.[7]

The elements of the dynamical matrix are defined by

$$D_{\alpha\beta}\left(\begin{matrix}l_3 & l_3'\\ k & k'\end{matrix}\middle|\vec{q}\right)=\exp\left\{-i\vec{q}\left[\vec{x}\begin{pmatrix}l_3\\k\end{pmatrix}-\vec{x}\begin{pmatrix}l_3'\\k'\end{pmatrix}\right]\right\}(m_k m_{k'})^{-1/2}$$
$$\times\sum_{ll'}\Phi_{\alpha\beta}\begin{pmatrix}l & l'\\ k & k'\end{pmatrix}$$
$$\times\exp\left\{-i\vec{q}\left[\vec{x}\begin{pmatrix}l_1\\l_2\end{pmatrix}-\vec{x}\begin{pmatrix}l_1'\\l_2'\end{pmatrix}\right]\right\}, \tag{6}$$

where the wave vector $\vec{q}$ refers to the two-dimensional Brillouin zone, and

$$\vec{x}\begin{pmatrix} l_1 \\ l_2 \end{pmatrix} = l_1\vec{a}_1 + l_2\vec{a}_2 \tag{7a}$$

describes the points of the two-dimensional infinite lattice and

$$\vec{x}\begin{pmatrix} l_3 \\ k \end{pmatrix} = l_3\vec{a}_3 + \vec{x}(k) \tag{7b}$$

describes the positions of the atoms within a "unit" cell, consisting of the sequence of unit cells of the original structure along the direction $\vec{a}_3$.

In what follows we are merely interested in the long-wavelength vibrations, e.g., $\vec{q} \sim 0$, so the exponential factors drop out.

The position vectors of the atoms and the dynamical matrix can be expressed in either of the above-mentioned coordinate systems $Oxyz$ (unprimed symbols) or $Ox'y'z'$ (primed symbols) by the same relations (6 and 7), provided the lattice primitive vectors $\vec{a}_i$ are expressed accordingly. In the system $Oxyz$ these vectors are given by the relation

$$\begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \\ \vec{a}_3 \end{pmatrix} = \frac{a}{2}\begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix}\begin{pmatrix} \vec{x}_0 \\ \vec{y}_0 \\ \vec{z}_0 \end{pmatrix}, \tag{8}$$

where a is the lattice constant.

The two representations of the dynamical matrix for $\vec{q}=0$ are related by the similarity transformation

$$D'(0) = TD(0)T^{-1}, \tag{9}$$

where T is an orthogonal matrix of the same order as D and whose elements are

$$T_{\alpha\beta}\begin{pmatrix} l_3 & l_3' \\ k & k' \end{pmatrix} = H_{\alpha\beta}\delta_{l_3 l_3'}\delta_{kk'}. \tag{10}$$

Using the corresponding point group G_0' of the above-defined space group G', we find that the interactions between the plane lattices are expressed for $\vec{q}=0$ by a matrix

$$D\begin{pmatrix} l_3 & l_3' \\ k & k' \end{pmatrix}$$

of the form

$$D\begin{pmatrix} l_3 & l_3' \\ k & k' \end{pmatrix} = \begin{bmatrix} A & B & -B \\ B & A & -B \\ -B & -B & A \end{bmatrix}. \tag{11}$$

Using the transformation (9) we obtain the diagonal form

$$D'\begin{pmatrix} l_3 & l_3' \\ k & k' \end{pmatrix} = \begin{bmatrix} A-B & 0 & 0 \\ 0 & A-B & 0 \\ 0 & 0 & A+2B \end{bmatrix}. \tag{12}$$

This form implies that the solutions for any slab having the above orientation are separated into two groups, one doubly degenerate containing the solutions corresponding to modes which vibrate in the two directions where the slab extends to infinity (xy modes), and one nondegenerate containing the solutions corresponding to vibrations perpendicular to the surfaces of the slab. This reduction by a factor of 3 of the dynamical matrix due to the orientation of the slab simplifies the computations.

For the purpose of comparing the frequencies of the above two types of solutions for a slab with the frequencies of an infinite lattice in the case of silicon, we calculated these frequencies on the basis of the following valence-force-field model. We assume only first-neighbor central interactions (force constant λ) and bond-bond interactions of the type proposed by Clark, Gazis, and Wallis[8] (force constant γ).

It is well known that such a model is inadequate to reproduce with accuracy the experimentally found dispersion curves for Si, because even a valence-force-field model with six parameters describing forces extended to the third neighbor gives higher frequencies for the acoustical branches.[9] As has been shown by Weber,[10] Coulomb interactions through charges localized on the bonds have to be introduced to describe properly the lowering and the flatness of these branches.

Nevertheless, we think that the proposed model is sufficient for the purpose of studying to a first approximation the effect of the finite size of the slab on the frequencies of vibrations. According to that model, the potential energy of the lattice is written as

$$\Phi = \frac{1}{2}\sum_{ij}\lambda(dr_{ij})^2 + \frac{1}{3!}\sum_{iji'}\gamma r_0^2(d\theta_{iji'})^2, \tag{13}$$

where the first sum extends over all first-nearest neighbors and the second sum over all angles of bonds for each atom.

Because the forces considered are extended only to second-nearest neighbors, it is evident that the interaction matrices

$$\Phi\begin{pmatrix} l_3 & l_3' \\ k & k' \end{pmatrix}$$

between the same pair of atoms k,k' are identical with those for the infinite structure, if at least one of the atoms lies at a distance from the surfaces of the slab greater than the thickness of the primitive unit cell measured perpendicular to the surface; i.e., only the forces exerted on the atoms on the first two lattice planes from the surfaces are perturbed if no change of equilibrium positions of the atoms due to the presence of the surface is assumed.

Finally, we note that the Brillouin zone corresponding to the slab structure is a section of the three-dimensional one for the fcc lattice through the center perpendicular to the vector $\vec{b}_3$.

III. RESULTS AND DISCUSSION

The values of the two parameters involved have been obtained by a fitting to the frequencies of the TO modes at the points Γ, X, and L of the infinite structure. The experimental values of these frequencies, the calculated ones, and the values of the parameters are given in Table I. The reason for using only the frequencies of the optical modes is that the frequencies of the acoustical modes at the points X and L are lower than predicted by such a model as discussed in the preceeding paragraph.

Using these values we have calculated the frequencies of the vibrational modes for slabs having thickness from 1 to 50 unit cells. The results obtained can be described as follows.

The xy modes, e.g., modes of $\vec{q}=0$ vibrating parallel to the surface of the slab, are grouped in two regions separated by a large gap which is almost equal to the gap between the TA and TO phonons of the point L of the three-dimensional structure. This means that all these modes should belong to the two branches of transverse phonons across the Λ direction. This is particularly true in the limit of a large number of cells across the z direction. For a slab having the thickness of only one cell, the gap is reduced by approximately 2 cm^{-1} from the three-dimensional one.

TABLE I. Transverse-optical frequencies for the points Γ, L, and X in the Brillouin zone (BZ).

Point in the BZ	TO frequencies(cm^{-1})[a] Experiment	Calculated
Γ	520	520
L	491	491.5
X	462	461.3

[a] Values of parameters used in the calculations: $\lambda=1.296$ mdyn/Å, $\gamma=0.047$ mdyn/Å.

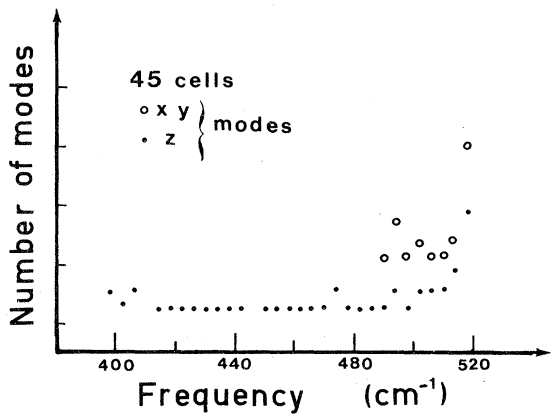

FIG. 2. Distribution of the optical in-plane modes: xy modes represented by O, and of out-of-plane modes: z modes represented by ● as a function of frequency.

All the modes of the upper group are of optical type, e.g., every pair of atoms in each cell moves in antiphase, while all the modes of the lower group are of acoustical type. The distribution of the "optical" modes shows two peaks near the limits of the frequency interval in which they are contained (Fig. 2). The distribution of the acoustical modes is rather constant, except near the

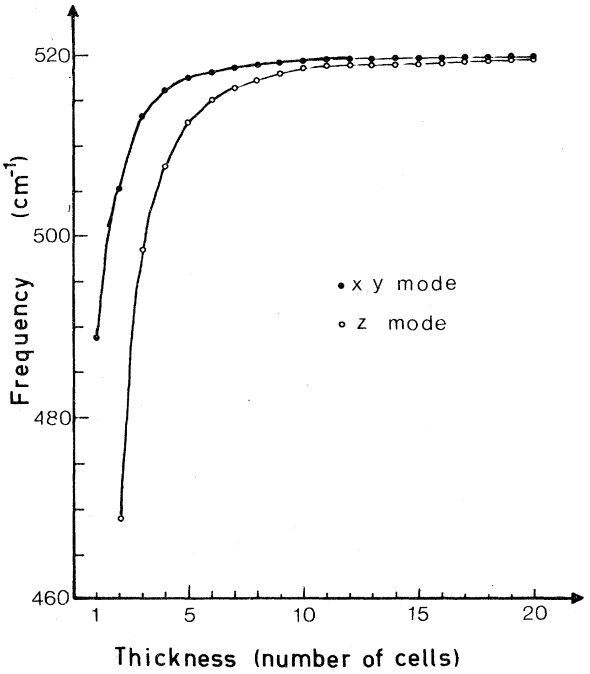

FIG. 3. Frequency variation of the higher-frequency optical mode for the xy modes as a function of the number of cells, i.e., thickness of the slab, rising exponentially toward the limit frequency of the Γ-point TO mode of the three-dimensional lattice. The higher-frequency z mode shows the same variation although lower in frequency.

upper end of the interval where it shows a peak.

The higher frequency of the optical modes corresponds to the one of the Γ point. For a slab having the thickness of only one cell, this frequency lies near the peak of the amorphous material spectrum and varies almost exponentially with the thickness towards the Γ frequency of the infinite lattice (Fig. 3).

The z modes, e.g., the modes whose displacements are along the z axis, have frequencies which are distributed between zero and the Γ-mode frequency, in two groups with a gap between them almost equal to the gap between the LO and LA frequencies of the point L of the three-dimensional lattice.

Again the vibrations of the higher-frequency group are of optical type and belong to the LO branch of the perfect crystal, while the vibrations of the lower-frequency group are of acoustical type, except the one with the higher frequency in this group which is again of optical type.

The distribution of the z modes of both types at the corresponding intervals is similar and is almost constant over the frequency range, showing only a peak at the upper end of the range.

The higher-frequency optical mode corresponds again to the Γ-point optical mode of the perfect crystal. The dependence of its frequency on the thickness of the slab is similar to that of the corresponding xy mode with the difference that the values are lower (Fig. 3).

Weighted frequency distributions of xy and z optical modes with a weighting factor inversely proportional to the thickness of the slab are shown in Fig. 4. For the case of very thin slabs 1 to 5 unit cells thick [Fig. 4(a)], the frequency distribution shows a pronounced maximum between 480–490 cm^{-1} near the maximum of the spectrum of amorphous material. Another less pronounced maximum occurs near the upper end. For the case of thicker slabs (11–15 unit cells thick) the frequency distribution of optical modes changes, showing the higher-frequency maximum more pronounced than the lower-frequency one [Fig. 4(b)]. Finally, the frequency distribution of even thicker slabs (21–25 unit cells thick) exhibits analogous features except that the higher-frequency maximum becomes more pronounced,

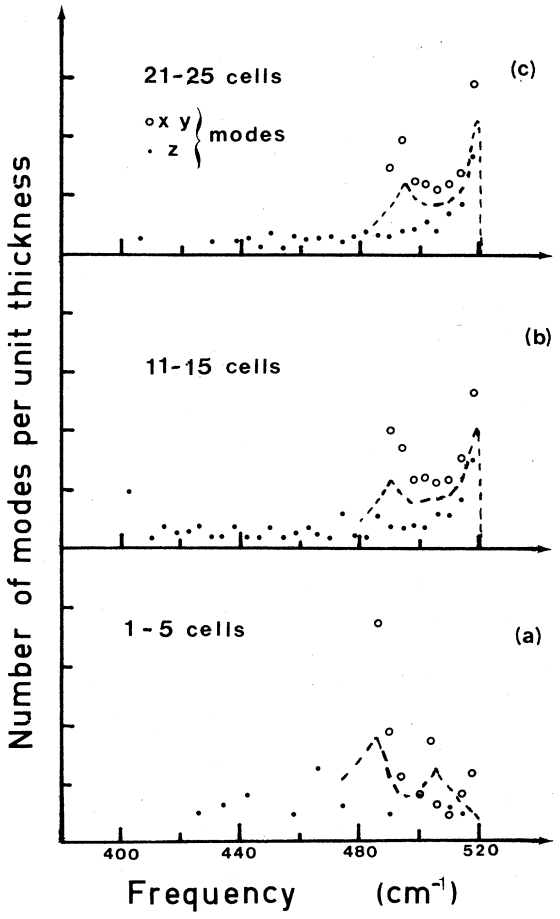

FIG. 4. Weighted frequency distributions of xy represented by O and z optical modes represented by ● with a weighting factor inversely proportional to the thickness of the slab. Number of modes per unit cell as a function of frequency. (a). For very thin slabs: 1 to 5 cells thick. (b). For slabs having a thickness of 11 to 15 cells. (c). For slabs 21 to 25 cells thick.

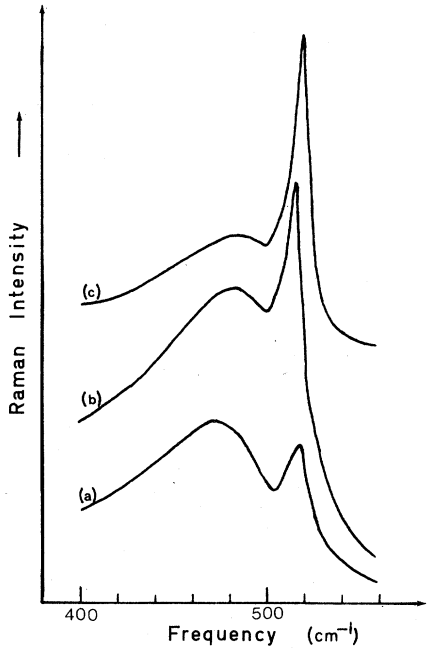

FIG. 5. Raman spectra of laser-annealed ion-implanted Si from three regions with partial recrystallization: (a), (b), and (c) partially recrystallized with grains of increasing size.

and the one at lower frequency is shifted to higher frequencies.

These features are exactly what has been observed in the Raman spectra of laser-annealed ion-implanted Si, in the intermediate recrystallization stage. These spectra can be explained if a distribution of very small crystallites of different sizes is assumed. As the distribution of crystallites moves towards larger sizes, the observed spectrum shifts from the one of the amorphous material to that exhibiting a second peak near the upper end, superimposed on the amorphous material spectrum and finally, to a spectrum showing only one peak of practically the same frequency as that of the perfect crystal, followed by a tail towards lower frequencies. This experimental results are summarized in Fig. 5.

IV. CONCLUSIONS

We have calculated the frequencies of the long-wavelength vibrations of thin slabs of silicon, parallel to the (111) plane, on the basis of a very simple valence-force-field model with two parameters for the purpose of studying the effect of the finite thickness of the slab on the vibrational frequencies of small homopolar crystals. We found that all of the modes belong to the certain branches of phonons of the perfect crystal, but have frequencies generally lower, depending on the thickness of the slab. Weighted frequency distributions of the optical-mode frequencies for slabs with different thicknesses display the main features of the Raman spectra of laser-annealed ion-implanted silicon when the recrystallization is imperfect.

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