Anisotropy in the electron inelastic scattering potential for plasmon excitation in silicon

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Both theoretical and experimental evidence have been put forward that plasmons have a detectable band structure. It would follow that the Fourier expansion of the combined plasmon and valence electron contribution to the electron inelastic scattering potential should have at least one nonzero coefficient for a reciprocal lattice vector $|\mathbf{G}|>0$. We calculate the $\mathbf{G}=2\pi/a(1,1,1)$ coefficient and demonstrate that it is indeed nonzero. This is a violation of a long held assumption that the plasmon and valence electron contribution to the inelastic scattering potential should be isotropic. [S0163-1829(97)00935-1]

Plasmons, even in periodic structures, are often treated as free oscillations. However, recent theoretical[1–3] and experimental[4] work on silicon shows that plasmons do in fact have a detectable band structure. Indeed, they obey, as would be expected for a collective electron excitation, the same crystal symmetry as an electron. For example, the plasmon dispersion curve shows a splitting at the L point and no splitting at the X point.[1,2] This plasmon band gap is attributable to a finite (nonzero) Fourier component of the crystal potential for higher-order coefficients. By extension the plasmon and valence electron contribution to the inelastic scattering potential can be calculated. In this paper we show how the potential is periodic by obtaining a finite (nonzero) higher-order Fourier component, $C^i_{0,\mathbf{G}}\neq 0$ for $\mathbf{G}=2\pi/a(1,1,1)$.

The optimal interpretation of results from high-energy electron microscopy and diffraction methods[5] is based on dynamical diffraction theory. In this a multiple scattering solution of a relativistic form of the Schrödinger equation is found when the crystal potential is expanded as a Fourier series.[6] In a rigorous treatment of inelastic electron-electron scattering one obtains a complex non-Hermitian ''correction matrix,'' which is added to the usual elastic scattering potential matrix.[7] This inelastic scattering potential matrix is analogous to the Fourier coefficients of the complex optical potential that is often used to characterize inelastic scattering phenomenologically.[8,9]

While a phenomenological absorption potential was first incorporated into electron diffraction theory by Slater[10] and Moliere,[11] it was first put on a substantial basis by Yoshioka.[7] Following Yoshioka we may write the total scattering potential in the form

$$V^S_{\mathbf{h},\mathbf{g}}=V_{\mathbf{h}-\mathbf{g}}+C_{\mathbf{h},\mathbf{g}}, \tag{1}$$

where $\mathbf{h},\mathbf{g}$ are reciprocal lattice vectors. $V_{\mathbf{h}-\mathbf{g}}$ are the usual local crystal potential Fourier components that result in elastic scattering. The $C_{\mathbf{h},\mathbf{g}}$ are complex nonlocal ''correction'' terms representing and incorporating the effects of excitations in the solid. That is, the $C_{\mathbf{h},\mathbf{g}}$ are the inelastic scattering potential matrix components. It is possible to explicitly separate $C_{\mathbf{h},\mathbf{g}}$ into two parts:

$$C_{\mathbf{h},\mathbf{g}}=C^r_{\mathbf{h},\mathbf{g}}+iC^i_{\mathbf{h},\mathbf{g}}. \tag{2}$$

$C^r_{\mathbf{h},\mathbf{g}}$ represents virtual inelastic scattering,[7,12] which may be interpreted as scattering to an excited state followed by further scattering back to the ground state, the net result contributing to the elastic wave train, while $C^i_{\mathbf{h},\mathbf{g}}$ represents real inelastic scattering. There are several contributions to $C_{\mathbf{h},\mathbf{g}}$, such as thermal diffuse (phonon) scattering (TDS), core excitation, and the plasmon and valence electron contribution, upon which this paper concentrates.

Until now, it has been held that the plasmon and valence electron contribution to the electron inelastic scattering potential matrix $C_{\mathbf{h},\mathbf{g}}$ was isotropic[9,13,14] — that all Fourier components were zero for $\mathbf{h},\mathbf{g}\neq 0$, as opposed to the highly localized core contribution or TDS contribution. For these highly localized potentials, the $\mathbf{G}=2\pi/a(1,1,1)$ contribution is nearly as large as the $\mathbf{G}=0$ contribution, as can be seen in Fig. 2. Due to this isotropic assumption, previous calculations of the effect of single particle or collective (plasmon) outer-shell valence electron excitations[9,13–16] and applications[17–19] have concentrated only on the inelastic mean inner potential $C^i_{0,0}$(plasmon) and/or the virtual mean inner potential $C^r_{0,0}$.

To solve for the off-diagonal scattering potential matrix components $C^i_{\mathbf{h},\mathbf{g}}$, $\mathbf{h}\neq\mathbf{g}$ is a computationally demanding calculation that is not yet practical. We can, however, make some approximations in considering terms of the form $C^{\mathbf{i}}_{0,\mathbf{G}}$, which are effectively the higher-order Fourier coefficients of the inelastic scattering potential. Recent calculations of the higher-order Fourier coefficients of the plasmon and valence contribution to the electron virtual scattering potential[20] show that $C^r_{0,\mathbf{G}}$ are clearly nonzero, at least for $\mathbf{G}=2\pi/a(1,1,1)$ in silicon, and in fact are larger than previous calculations of the supposedly dominant core

contribution.[13] We calculate here the equivalent contribution to real inelastic scattering from plasmons and valence electrons in silicon.

The valence electron excitation potential is strongly dependent on the electronic band structure of the solid. It is therefore convenient to represent the valence electron and plasmon excitation contribution $C^i_{0,\mathbf{G}}(\text{plasmon})$ to the total $C^i_{0,\mathbf{G}}$, in terms of the wave-vector and frequency-dependent dielectric matrix $\varepsilon_{\mathbf{h,g}}(\mathbf{q},\omega)$ (see, for example, Ref. 15),

$$C^i_{0,\mathbf{G}}(\text{plasmon}) = 4\pi e^2 \int_0^{E^0/\hbar} d\omega \sum_{\mathbf{G}'} \times \int_{BZ} \frac{d\mathbf{q}'}{(2\pi)^3} \frac{i}{2|\mathbf{q}'+\mathbf{G}'||\mathbf{q}'+\mathbf{G}+\mathbf{G}'|} \times [\varepsilon^{-1}_{\mathbf{G}',\mathbf{G}+\mathbf{G}'}(\mathbf{q}',\omega) - \varepsilon^{*-1}_{\mathbf{G}+\mathbf{G}',\mathbf{G}'}(\mathbf{q}',\omega)] \times \delta\left(\omega - (\mathbf{q}'+\mathbf{G}')V + \frac{\hbar(\mathbf{q}'+\mathbf{G}')^2}{2m}\right), \quad (3)$$

where $\mathbf{G}'$ and $\mathbf{G}$ are reciprocal lattice vectors, $E^0=\hbar\omega$ is the incident electron energy, V is the incident electron velocity, and m is the electron mass. We note that $\varepsilon^{-1}_{\mathbf{0,G}}(\mathbf{q},\omega)$ is the $(0,\mathbf{G})$ element of the inverse of the entire dielectric matrix, containing all the elements $\varepsilon_{\mathbf{h,g}}(\mathbf{q},\omega)$.

For a centrosymmetric crystal structure such as silicon, assuming isotropic dielectric response, and using the approximation[15] $\varepsilon^{-1}_{0,\mathbf{G}}(\mathbf{q}'+\mathbf{G}',\omega) = \varepsilon^{-1}_{\mathbf{G}',\mathbf{G}'+\mathbf{G}}(\mathbf{q}',\omega)$, we may express the higher-order Fourier coefficients of the electron inelastic scattering potential in terms of the generalized higher-order loss function $\text{Im}\{-\varepsilon^{-1}_{0,\mathbf{G}}(|\mathbf{q}|,\omega)\}$,

$$C^i_{0,\mathbf{G}} = \frac{e^2}{\pi V} \int_0^{E^0/\hbar} d\omega \int_{q(\theta_{\min})}^{q(\pi)} \frac{d|\mathbf{q}|}{|\mathbf{q}+\mathbf{G}|} \text{Im}\{-\varepsilon^{-1}_{0,\mathbf{G}}(|\mathbf{q}|,\omega)\}. \quad (4)$$

The $|\mathbf{q}|$ integration is over the range defined by some minimum possible scattering angle $\theta_{\min}\to 0$ through to $\theta=\pi$, and the ω limits run over all possible energy transfers to the solid. We note that the inelastic mean inner potential is obtained by setting $\mathbf{G}=0$ in Eq. (4), as first derived by Pines[21] (see also Ritchie and Howie.[22]) We make no mention of a ''cut-off wave vector'' (the wave vector $\mathbf{q}_c$ above which collective excitations cease to exist) in this formalism as the collective excitations are correctly attenuated in the dielectric loss function. This calculation sums over all possible single-particle excitations, which collectively add to produce a plasmonlike resonance in the loss function. We shall refer to this resonance as a plasmon throughout this work.

In this work we consider the random-phase-approximation dielectric matrix obtained by Adler[23] and Wiser:[24]

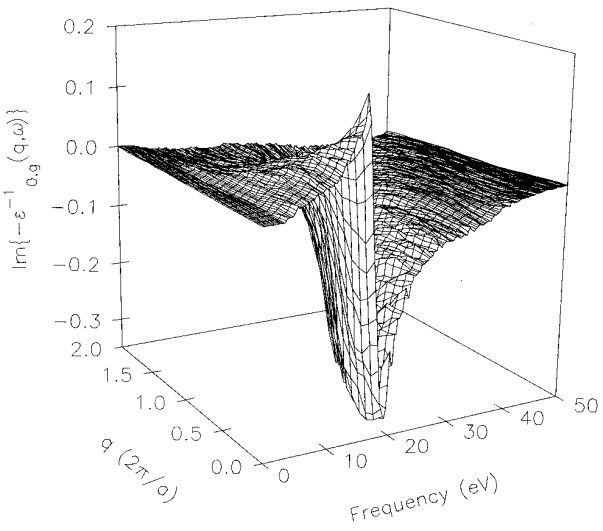

FIG. 1. The higher-order loss function $\text{Im}\{-\varepsilon^{-1}_{0,\mathbf{G}}(|\mathbf{q}|,\omega)\}$, $\mathbf{G}=(2\pi/a)(1,1,1)$ for silicon as a function of wave vector and frequency.

$$\varepsilon_{\mathbf{h,g}}(\mathbf{q},\omega) = \delta_{\mathbf{g,h}} - \frac{4\pi e^2}{\Omega|\mathbf{q}+\mathbf{g}||\mathbf{q}+\mathbf{h}|} \lim_{\alpha\to 0^+} \times \sum_{k,n,n'} \frac{f_0[E_{n'}(\mathbf{k}+\mathbf{q})] - f_0[E_n(\mathbf{k})]}{E_{n'}(\mathbf{k}+\mathbf{q}) - E_n(\mathbf{k}) + \hbar\omega + i\hbar\alpha} \times \langle \mathbf{k}+\mathbf{q}, n' | e^{i(\mathbf{q}+\mathbf{g})\cdot\mathbf{r}} | \mathbf{k}, n\rangle \times \langle \mathbf{k}, n | e^{-i(\mathbf{q}+\mathbf{h})\cdot\mathbf{r}} | \mathbf{k}+\mathbf{q}, n'\rangle, \quad (5)$$

where Ω is the crystal volume, $f_0(E)$ is the Fermi function, and n,n' are the band indices, labeling the Bloch states $|\mathbf{k},n\rangle$ of energy $E_n(\mathbf{k})$ in the solid. A nonlocal empirical pseudopotential calculation based on the work of Cohen and Chelikowsky[25] is used to obtain the electronic states in Eq. (5). A pseudopotential method has been chosen as this efficiently gives a very accurate representation of the higher conduction bands, upon which the loss function is highly sensitive. Full details of the calculation of the dielectric matrix can be found in Forsyth, Josefsson, and Smith.[1]

Figure 1 shows the higher-order loss function for silicon [based on the dielectric matrix of Eq. (5)] up to an energy of 50 eV, for $|\mathbf{q}|$ between 0 and $4\pi/a$, with $\mathbf{G}=2\pi/a(1,1,1)$. It has a similar form to that obtainable from a simple two-band plasmon model.[4]

Figure 2 shows the magnitude of the Fourier coefficients $C^i_{0,\mathbf{G}}(\text{plasmon})$ and $C^i_{\mathbf{0,0}}(\text{plasmon})$ as functions of incident energy, based on Eq. (4). Also shown are the equivalent Fourier coefficients of the contribution to the core excitation potential from K-shell ionization[26–28] and thermal diffuse scattering[29] (TDS) at 100 K. We note that for the plasmon, core, and TDS potentials $C^i_{0,\mathbf{G}}$, $\mathbf{G}=2\pi/a(1,1,1)$ has the opposite sign to $C^i_{0,0}$. This is a geometrical effect, and is expected for a crystal with zinc-blende symmetry, as the structure factor for $\mathbf{G}=2\pi/a(1,1,1)$ is of opposite sign to the structure factor for $\mathbf{G}=0$. The $C^i_{0,\mathbf{G}}$ (K-shell) coefficients were calculated based on a screened hydrogenic model for the tightly bound core state, integrating over all orthogonal

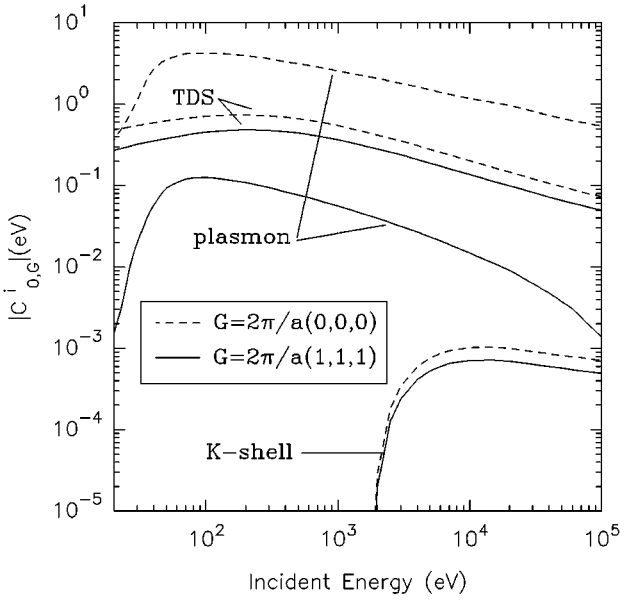

FIG. 2. Variation of $|C^i_{0,\mathbf{G}}(\text{plasmon})|$ with incident electron energy for $\mathbf{G}=(2\pi/a)(1,1,1)$ and $\mathbf{G}=(2\pi/a)(0,0,0)$ as determined by Eq. (4). Note that $C^i_{\mathbf{0,0}}$ is the mean inner potential of (Ref. 15). For comparison, $|C^i_{0,\mathbf{G}}(K\text{ shell})|$ (Refs. 26–28), and $|C^i_{0,\mathbf{G}}\text{ (TDS)}|$ (Ref. 29) have been included. For the plasmon, TDS, and K shell potentials $C^i_{0,\mathbf{G}}$, $\mathbf{G}=2\pi/a(1,1,1)$ has the opposite sign to $C^i_{0,0}$. The TDS potential is calculated at 100 K.

continuum final states. The details of this calculation have been discussed in detail elsewhere.[26–28] The TDS potential is calculated via the Einstein independent oscillators model, as described in Allen and Rossouw.[29] Core electron excitations (as with phonon excitations) are generally associated with large momentum transfers and highly localized inelastic scattering potentials in real space. The magnitude of the corresponding higher-order Fourier coefficients $C^i_{\mathbf{0,G}}(\text{core})$ of these potentials are therefore relatively large in comparison with the contribution of the mean-inner-potential $C^i_{\mathbf{0,0}}(\text{core})$.[13] The importance of this for analytic electron diffraction and microscopy has been discussed at length elsewhere.[27,30–32] The higher-order coefficients play a large part in determining such quantities as image contrast. As collective electronic or plasmon excitations are associated with a relatively small momentum transfer and states that are poorly localized in real space, they are expected to result in a highly delocalized inelastic scattering potential with $C^i_{\mathbf{0,G}}(\text{plasmon}) \ll C^i_{0,0}(\text{plasmon})$. Indeed, the inelastic scattering potential due to plasmon excitation is delocalized, as the ratio of $C^i_{0,\mathbf{G}}(\text{plasmon})$ to $C^i_{\mathbf{0,0}}(\text{plasmon})$ is of the order of 10^{-2}. However, the present results clearly indicate that the plasmon and valence electron excitation contribution to the higher-order Fourier coefficients of the inelastic scattering potential are not negligible, at least for $\mathbf{G}=2\pi/a(1,1,1)$. At energies up to 100 keV, the higher-order plasmon contribution to the scattering potential is larger than the K-shell contribution, and within an order of magnitude of the TDS contribution.

The assumption that the inelastic scattering potential due to plasmon excitation is isotropic leads to plasmons that are completely delocalized. The localization of a potential can be considered as the weighting of the Fourier components of the potential in reciprocal space. With only one nonzero coefficient for $|\mathbf{G}|>0$ we cannot discuss the localization with any certainty, but our results indicate that the potential is not completely delocalized. This is consistent with recent theoretical[33–35] and experimental evidence of plasmon localization.[36,37]

In conclusion, this work presents a rigorous calculation of the $\mathbf{G}=2\pi/a(1,1,1)$ Fourier coefficient of the contribution to the electron inelastic scattering potential due to plasmon and valence electron excitations in silicon. This is based on a nonlocal electronic band-structure-dependent dielectric matrix calculation. Previous work[9,13,15,16] has concentrated on the inelastic mean inner potential $C^i_{0,0}(\text{plasmon})$, in the belief that the higher-order Fourier coefficients $C^i_{\mathbf{0,G}}(\text{plasmon})$ would be negligible. However, the results presented here show that the contribution of $C^i_{0,\mathbf{G}}(\text{plasmon})$ to the total electron inelastic scattering potential is greater than that due to the K-shell ionization potential for $\mathbf{G}=2\pi/a(1,1,1)$, and within an order of magnitude of the contribution to the potential from TDS at 100 K. This result is consistent with the recent experimental evidence[36,37] that plasmons are more localized than previously expected.

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[1] A. J. Forsyth, A. W. Josefsson, and A. E. Smith, Phys. Rev. B **54**, 14 355 (1996).
[2] R. Daling, W. Van Haeringen, and B. Farid, Phys. Rev. B **44**, 2952 (1991); **45**, 8970 (1992).
[3] K. Sturm and W. Schulke, Phys. Rev. B **46**, 7193 (1992).
[4] W. Schulke and A. Kaprolat, Phys. Rev. Lett. **67**, 879 (1991).
[5] *Electron Diffraction Techniques*, edited by J. M. Cowley (Oxford University Press, Oxford, 1993).
[6] H. A. Bethe, Ann. Phys. (Leipzig) **87**, 55 (1928).
[7] H. Yoshioka, J. Phys. Soc. Jpn. **12**, 618 (1957).
[8] D. M. Bird and Q. A. King, Acta Crystallogr. Sect. A **46**, 202 (1990).
[9] G. Radi, Z. Phys. **212**, 146 (1968); **213**, 244 (1968); Acta Crystallogr. Sect. A **26**, 41 (1970).
[10] J. C. Slater, Phys. Rev. **51**, 840 (1937).
[11] K. Moliere, Ann. Phys. (Leipzig) **34**, 461 (1939).
[12] Z. L. Wang, Acta Crystallogr. Sect. A **46**, 366 (1990).
[13] P. Rez, Acta Crystallogr. Sect. A **34**, 48 (1978).
[14] M. J. Whelan, J. Appl. Phys. **36**, 2099 (1965).
[15] T. W. Josefsson and A. E. Smith, Phys. Rev. B **50**, 7322 (1994).

[16] T. W. Josefsson and A. E. Smith, Phys. Lett. A **180**, 174 (1993).
[17] T. W. Josefsson, R. L. Cobal, and L. J. Allen, Phys. Rev. B **54**, 12 873 (1996).
[18] L. M. Peng, S. L. Dudarev, and M. J. Whelan, Phys. Lett. A **175**, 461 (1993).
[19] S. L. Dudarev, L.-M. Peng, and M. J. Whelan, Phys. Rev. B **48**, 13 408 (1993).
[20] A. J. Forsyth, A. E. Smith, and T. W. Josefsson, Acta Crystallogr. Sect. A **53**, 523 (1997).
[21] D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, New York, 1960).
[22] R. H. Ritchie and A. Howie, Philos. Mag. **36**, 463 (1977).
[23] S. L. Adler, Phys. Rev. **126**, 413 (1962).
[24] N. Wiser, Phys. Rev. **129**, 62 (1963).
[25] M. L. Cohen and J. R. Chelikowsky, *Electronic Structure and Optical Properties of Semiconductors*, 2nd ed. (Springer-Verlag, Berlin, 1989).
[26] V. M. Maslen, J. Phys. B **16**, 2065 (1983).
[27] L. J. Allen and C. J. Rossouw, Phys. Rev. B **47**, 2446 (1993).
[28] L. J. Allen and T. W. Josefsson, Phys. Rev. B **52**, 3184 (1995).
[29] L. J. Allen and C. J. Rossouw, Phys. Rev. B **39**, 8313 (1989).
[30] Z. L. Wang, *Elastic and Inelastic Scattering in Electron Diffraction and Imaging* (Plenum Press, New York, 1995).
[31] L. J. Allen, T. W. Josfsson, and C. J. Rossouw, Ultramicroscopy **55**, 258 (1994).
[32] W. Nuchter and W. Sigle, Philos. Mag. A **71**, 2165 (1995).
[33] K. Sturm, Adv. Phys. **31**, 1 (1982).
[34] H. Kohl, Ultramicroscopy **11**, 53 (1983).
[35] K. Kohl and H. Rose, Adv. Electron. Electron Phys. **65**, 173 (1985).
[36] D. A. Muller and J. Silcox, Ultramicroscopy **59**, 195 (1995).
[37] Z. L. Wang and A. J. Shapiro, Ultramicroscopy **60**, 115 (1995).