PHYSICAL REVIEW B VOLUME 38, NUMBER 18 15 DECEMBER 1988-II

Optical properties of metallic silicon

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(Received 16 August 1988)

The optical reflectivity of polycrystalline Si in the metallic β-tin-type, primitive hexagonal (ph), and hcp high-pressure phases has been measured from 0.5 to 4 eV. Distinct changes of the reflectivity are observed at the structural phase transitions. The optical response of ph-Si is investigated in detail, and the dominant absorption near 2.5 eV is explained in terms of parallel band transitions characteristic of a polyvalent, nearly-free-electron metal. An *ab initio* band-structure calculation of ph-Si by means of the linear-muffin-tin-orbital method is used to also calculate the interband dielectric function. The calculated optical response is found to be in excellent agreement with the experimental data.

Extensive experimental and theoretical studies of the structural phase transitions in silicon under pressure have been performed in recent years. With increasing pressure, the structural sequence is cubic diamond to β-Sn at ~ 11 GPa,[1] to primative hexagonal (ph) at 13–16 GPa,[2,3] to an intermediate phase at ~ 37 GPa,[3] to hexagonal-close-packed (hcp) at ~ 40 GPa,[3,4] and finally to face-centered cubic (fcc) at ~ 78 GPa.[5] "First-principles" calculations of the phase stability of Si (see,e.g., Refs. 6–9) have proved to be sufficiently accurate to predict transition volumes and pressures in good agreement with experiment. Furthermore, the theoretical studies elucidate the mechanism of the β-Sn$\rightarrow$ph and ph$\rightarrow$hcp transitions in terms of the associated soft-phonon behavior. Experimental investigations of the physical properties of the high-pressure metallic phases of Si have mainly been concerned with superconducting properties,[10–14] where a maximum T_c of ~ 8 K is found in the vicinity of the β-Sn$\rightarrow$ph transition.

In this paper we report on an experimental and theoretical investigation of the optical response of polycrystalline metallic silicon. The optical reflectivity of Si in the β-Sn, ph, and hcp phases has been measured at pressures of up to 44 GPa and shows distinct changes at the phase transitions. Due to its relatively large stability range, the ph phase was chosen for a more detailed investigation. The optical absorption in the ph phase as derived from an analysis of the reflectivity spectra shows a pronounced structure in the visible spectral range which is attributed to interband transitions. Within the framework of elementary pseudopotential theory we show that the optical properties of ph-Si are consistent with the characteristic features of the optical response of a polyvalent nearly-free-electron (NFE) metal. In other words, the dominant optical absorption of ph-Si can be explained in terms of excitations between parallel bands which arise from band splitting along those Bragg planes cutting through the Fermi sphere.[15–17] In this respect the most celebrated example is the optical response of Al,[16] which is the neighboring trivalent element of Si in the Periodic Table. A more detailed analysis of the optical response of ph-Si is performed in terms of a full theoretical calculation of the interband dielectric function based on an *ab initio* linear-muffin-tin-orbital (LMTO) calculation of the band structure. The calculated transition energies as well as the strength of the optical excitations are found to be in excellent agreement with the experimental data.

Reflectivity measurements under pressure were performed by using the gasketed-diamond-window-cell technique in combination with a micro-optical system for the spectral range from 0.5–~ 4 eV.[18] Pressures were determined from the red shift of the ruby luminescence.[19] A piece of single-crystal silicon (thickness 25 μm) was placed on one of the diamond windows, and the remaining volume of the gasket hole was filled with KCl. The absolute reflectivity at near-normal incidence (denoted as R_d) was measured at the diamond-sample interface from focal spots of about 30 μm diam. The R_d spectra reported below are corrected for absorption in the diamond window and for reflection losses at its external surface. More details of the experimental technique are given elsewhere.[18,20] Reflection spectra may be affected by preferred orientation effects due to the use of single-crystal starting material or due to a nonisotropic stress component acting on the sample. However, very similar results were obtained with powder samples and, furthermore, the changes in reflectivity were reversible upon releasing pressure (except for hysteresis effects near phase transitions).

Reflectance spectra of polycrystalline Si at four different pressures corresponding to the diamond, β-tin, ph, and hcp phases, respectively, are shown in Fig. 1(a). The three metallic phases exhibit a high reflectivity in the near-infrared spectral range followed by a decrease towards the visible range, which we attribute to interband absorption. Obviously, the visible interband absorption is strongest in the β-tin and ph phases and decreases in the hcp phase, but shows structure for all three phases.

The variation with pressure of the reflectivity in the ph phase has been studied in more detail. Another reflectivity spectrum of ph-Si at 17.5 GPa, i.e., just above the β-tin–to–ph transition, is shown in Fig. 1(b). Comparing the spectra for ph-Si in Figs. 1(a) and 1(b), only

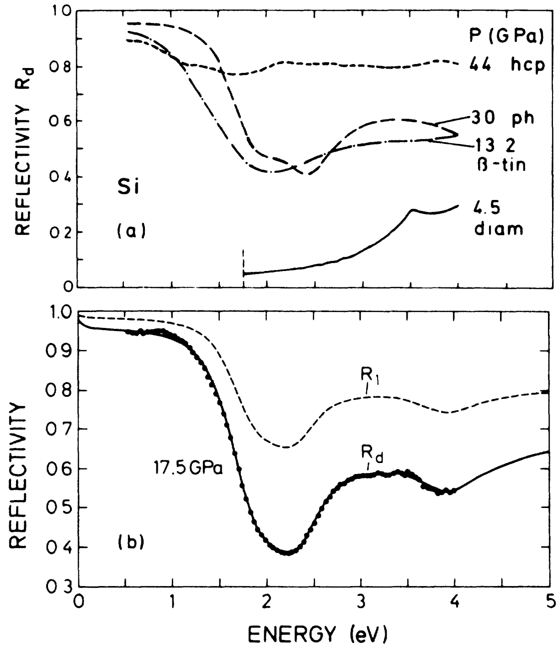

FIG. 1. (a) Reflectivity spectra (R_d) of silicon in the diamond, β-tin, primitive hexagonal, and hcp phase at 4.5, 13.2, 30, and 44 GPa, respectively. (b) Reflectivity of primitive hexagonal silicon at 17.5 GPa. Closed symbols represent a selection of experimental data points (R_d). The solid line corresponds to the result of a least-squares fit (see text for details) to the experimental data. The dashed line is the reflectivity R_1 calculated for a hypothetical sample-vacuum interface.

small changes of the reflectivity are found over the stability range of the ph phase, for which the total change in specific volume is about 10%. With increasing pressure one observes a small splitting of the reflectivity minimum centered at 2.2 eV.

In order to derive the dielectric function $\epsilon(\omega)$ from the reflectivity data, we calculate the normal incidence reflectivity R_d from an oscillator expression for $\epsilon(\omega)$ using the Fresnel equation and then fit R_d to the experimental data. For $\epsilon(\omega)$ we use a Drude expression with scattering time τ_D plus a superposition of contributions from "parallel band" oscillators[16] at resonance energy ω_k and with strength A_k and interband scattering time τ_k. We require that the imaginary part $\epsilon_2(\omega)$ obey the optical sum rule for four valence electrons per atom (see Ref. 16 for details). Figure 1(b) shows a typical result of a least-squares fit of the model dielectric function and the related reflectivity to the experimental data at 17.5 GPa. Also shown in Fig. 1(b) is the corresponding reflectivity R_1 for a hypothetical sample-vacuum interface.

Figure 2(a) shows the interband part of $\epsilon_2(\omega)$ of Si at 13.2 GPa in the β-tin and at two pressures in the ph phase. At low energy, an unambiguous separation into intraband and interband absorption is not possible, but this does not affect the main features of the optical-interband absorption in the visible spectral range. The dominant absorption near 2.5 eV has a low-energy shoulder which is resolved only at pressures above 24 GPa. A weaker absorption is seen at the high-energy limit of the experiment near 4 eV. Figure 3 gives the pressure depen-

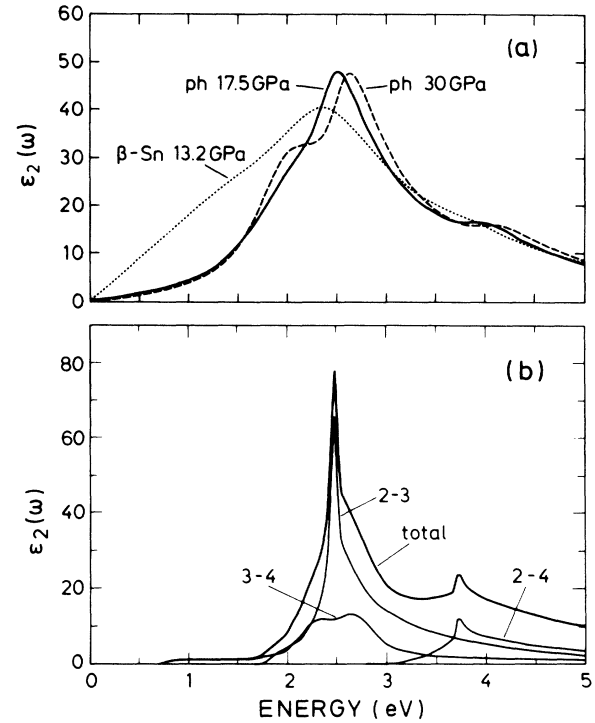

FIG. 2. (a) Interband dielectric function $\epsilon_2(\omega)$ (imaginary part) of silicon at different pressures as derived from the reflectivity spectra. (b) Calculated polarization-averaged interband dielectric function $\epsilon_2(\omega)$ of primitive hexagonal silicon at $V/V_0=0.65$ ($P_{\mathrm{calc}}=22.2$ GPa) with decomposition of $\epsilon_2(\omega)$ into various interband contributions. The numbers indicate initial- and final-state bands. The bands are enumerated in the sequence of increasing energy.

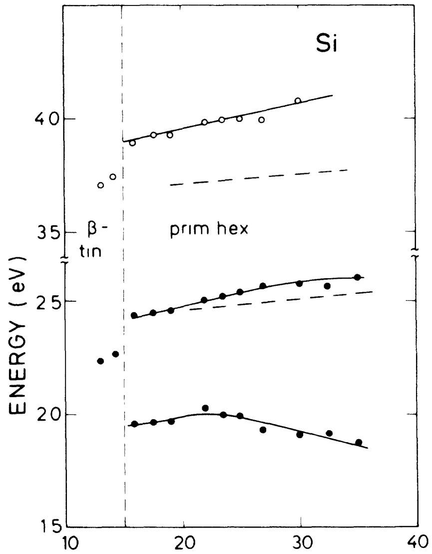

FIG. 3. Experimental optical-transition energies in metallic silicon (symbols) as a function of pressure. The solid lines are a guide to the eye. The dashed lines represent energies of peaks in the calculated interband dielectric function as a function of calculated pressure.

dence of the corresponding resonance energies $\hbar\omega_k$.

As a first approach to explain the origin of the optical-absorption features we use a NFE picture. The Fermi surface of ph-Si cuts through reciprocal lattice planes corresponding to the reciprocal lattice vectors $\mathbf{G}=[001]$, [100], and [101]. The splitting into parallel bands along these planes is expected to result in Van Hove singularities of the unbroadened joint density of states for direct optical transitions.[15–17] Within a two-plane-wave approximation one can estimate the band splitting $2|U_G|$ from the relevant Fourier coefficients U_G of the pseudopotential. Using the screened empty-core pseudopotential form factor of Si (Ref. 21) the predicted band splittings at a relative volume $V/V_0=0.64$ ($\mathbf{P}_{\mathrm{expt}}\approx 22$ GPa) are $2|U_G|\approx 1.45$, 0, and 2.8 eV for the (001), (100), and (101) planes, respectively. The multiplicity of the planes as well as $2|U_G|$ enters into the strength of the parallel-band absorption.[16] Hence, one expects one strong optical transition in the visible spectral range at about 2.8 eV. Furthermore, with decreasing volume the form factor for a given $\mathbf{G}$ increases[20] so that the predicted (101) splitting is also expected to increase with pressure. This suggests to assign the 2.5-eV transition (see Fig. 3) to transitions between parallel bands along (101) planes. We note that these transitions also give a dominant contribution to the optical absorption of hcp zinc being a divalent NFE metal.[17]

The crude NFE model accounts for the energy of the dominant optical transition, in reasonable agreement with the experimental data. It is tempting to associate the shoulder in the absorption spectra at slightly lower energy (~ 2 eV) to the weaker absorption at (001) planes, in particular, because it shifts to lower energy with increasing pressure.[22] This would be expected from the pseudopotential band splittings for (001) planes, because $|\mathbf{G}_{001}|$ is smaller than the wave vector corresponding to the zero crossing of the form factor. This assignment, however, is not supported by the band-structure calculations reported below. These calculations also provide an interpretation of the absorption near 4 eV, which cannot be explained within the two-plane-wave approximation. We note from Fig. 1(a) that obviously the interband absorption in hcp-Si is weaker compared to ph-Si. Within the NFE model discussed above this is explained by the fact that the important band splitting along the (101) planes of hcp-Si is predicted to be less than half of that along (101) in ph-Si.

Band-structure calculations for the primitive hexagonal cell were performed by using the self-consistent scalar-relativistic LMTO method in the atomic-sphere approximation (ASA), with the so-called "combined correction" properly included.[23] We consider a frozen-core charge density and treat the $3s^2p^2$ states as band electrons. The structure of ph-Si is rather open. Therefore, we introduce two empty spheres positioned at $(2a/3,a/3,c/2)$ and $(a/3,2a/3,c/2)$ in the primitive cell. This makes the structure more closely packed and the charge density in the interstitial region is properly described. The exchange-correlation potential was used within the local-density formalism.[24] The self-consistency is obtained after several iterations with a mesh of 726 $\mathbf{k}$ points in the irreducible part of the Brillouin zone (IBZ).

The calculated band structure of ph-Si is shown in Fig. 4. Panels 4(a) and 4(b) give the band structure at $V/V_0=0.65$ ($P_{\mathrm{calc}}=22.3$ GPa). The dispersion along Γ-*L*-*H*-Γ, which is of particular interest for the discussion of the optical response, is also shown for $V/V_0=0.59$ ($P_{\mathrm{calc}}=42.6$ GPa). Obviously, the bands of ph-Si have the characteristic features of a NFE metal showing small (compared to E_F) parallel band splittings. The splitting along *M*-*K*-Γ corresponds to the (100) reciprocal lattice planes, along *A*-*L* and *A*-*H* to the (001) planes, and the directions Γ-*L* and Γ-*H* lie close to the (101) planes. Along *L*-*H* we have a more complicated situation due to the mixing of parallel bands from all three relevant reciprocal lattice planes.

The self-consistent eigenvalues and eigenvectors from the LMTO band structure are used to calculate the interband imaginary part of the dielectric function in the limit of vanishing line width.[25] The matrix elements of the momentum operator between occupied and unoccupied states were evaluated for $\hbar\omega\leq 5$ eV with the wave functions expressed in terms of the one-center expansion.[23] The $\mathbf{k}$-space integration is performed using the tetrahedron method[26] based in the same $\mathbf{k}$ points in the IBZ as for the self consistency of the band structure.

The interband dielectric function calculated for polar-

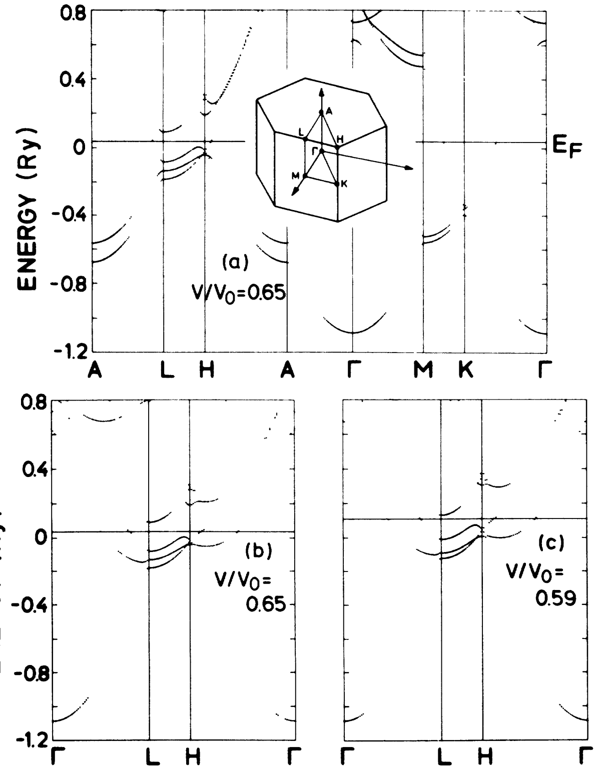

FIG. 4. (a) LMTO band structure of primitive hexagonal silicon at $V/V_0=0.65$. (b) Same as (a) for other directions. (c) Same as (b) for $V/V_0=0.59$.

ization parallel and perpendicular to the c axis shows some differences which, however, are not important for our present discussion. The polarization-averaged $\epsilon_2(\omega)$ is shown in Fig. 2(b), which also gives the decomposition of $\epsilon_2(\omega)$ into contributions from various pairs of bands. The absolute magnitude of $\epsilon_2(\omega)$ agrees well with the experimental data, if one takes into account that lifetime broadening is neglected in the theoretical calculation. The dominant contribution near 2.6 eV is mainly due to transitions between bands 2 and 3 and corresponds to the (101) splitting. The second weaker contribution near this energy is due to transitions between bands 3 and 4. The energy, however, does not correspond to the (001) splitting, because the absorption mainly involves states along the *L*-*H* direction, where the band splittings are a result of mixing of states from (001), (100), and (101) planes. The peak in ϵ_2 near 3.7 eV, which arises from transitions between bands 2 and 4, is also due to parallel bands near the *L*-*H* direction. Since the (100) splitting is very small (see Fig. 4), weak structureless interband absorption extends down to low energy.

In conclusion, we have determined the optical absorption of Si in metallic high-pressure phases from 0.5 to 4 eV at pressures up to 44 GPa by analyzing reflectivity spectra. In focusing our attention to ph-Si and by referring to an elementary pseudopotential model we find that the optical response is a spectroscopic manifestation of the NFE-like behavior of metallic Si. In other words, the free-electron bands are only weakly perturbed by Bragg reflection planes, in striking contrast to the covalently bonded diamond-type phase of Si. Using a realistic band structure of ph-Si obtained by means of the LMTO method, we have calculated the optical interband absorption. These theoretical results facilitate a more detailed interpretation of the experimental optical response. Moreover, the calculated optical properties are found to be in excellent agreement with the experimental data presented here.

ACKNOWLEDGMENT

We acknowledge the contributions of H. G. Zimmer, who was involved in preliminary experimental work. We thank Mrs. R. Hempel for technical assistance.

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