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Cathodoluminescence of silicon in the visible–ultraviolet region

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Here we report cathodoluminescence (CL) spectra of single-crystal silicon over the wavelength interval 250–600 nm. We verify the existence of luminescence from Si in the visible–ultraviolet region with improved experimental conditions. The most prominent features of the CL spectra are the two peaks at 310 and 390 nm. These are intrinsic to Si, and have been assigned to proper optical transitions between the valence and conduction bands. The correlation with the absorption structure is good, and a comparison of Si CL and absorption spectra reveals that the emission spectrum shift, $\sim$0.2 eV toward lower energy relative to the absorption spectrum. These emissions are insensitive to dopants ($\sim 10^{18}$-cm^{-3} phosphorus donors or boron acceptors) and crystallographic orientation. Bombardment with electrons decreases the intensity of the emissions. [S0163-1829(98)06119-0]

I. INTRODUCTION

The luminescence of semiconductors has been explored in many papers,[1–8] in which most of the attention is given to the fundamental edge. These studies render information about free carriers,[1–3] lattice vibrations,[2–4] electron-phonon interactions,[5–7] band-to-impurity-level transitions, and the decay of a free or bound exciton.[2,3,8] In the wide energy region above the absorption edge up to the vacuum-ultraviolet region, semiconductors strongly absorb photons, mainly due to direct-interband transitions. Thus the optical spectrum in that energy region is helpful in understanding the energy-band structure. In the past, almost all information concerning the energy-band structure of semiconductors was obtained by optical-absorption studies and theoretical calculations.[9–12] For the short-wave side of the absorption edge, the value of the absorption coefficient rises rapidly,[13,14] and it is difficult to measure the absorption spectrum directly. Then the absorbing properties of semiconductors are determined from the reflectivity,[15–18] photoemission[19–21] spectra, and Kramers-Kronig relations. In contrast to the reflectivity spectrum, the optical-absorption spectrum is a derived, not a measured, quantity. Also, the results obtained by Kramers-Kronig analysis of reflectance measurements often show effects due to improper extrapolations. Photoemission spectroscopy is a very sophisticated technique, but the resolution of the photoemission spectrometer is usually $\geqslant$0.2 eV, which is rather lower than the optical measurement. Hence, as compared with reflectivity and photoemission, optical emission measurement can provide information about transitions not only directly, but also more accurately and conveniently. Thus it is a powerful method to study the energy levels, electron and hole state distribution functions, and unoccupied electronic states.[22] However, progress in studies of the luminescence of semiconductors above the fundamental edge is slow, because of the low luminescence efficiency. Fortunately, the intensity of the luminescence produced by electron excitation is normally considerably greater than that induced by ultraviolet light, and weak luminescence can be measured with extremely efficient light detection techniques, like photon counting. An account of cathodoluminescence (CL) studies of Ge in the visible region has appeared in the literature.[23]

We have also reported on the emission spectra from Si and Ge by electron impact in a wider spectral range, i.e., the visible–ultraviolet region.[24,25] It is of interest to note that the spectrum peaks of Si occur in the region where the extinction coefficient decreases steeply.[24] However, at the same time, the optical yield produced by fast electrons from a ^{90}Sr β source was much lower. For obtaining good statistics about the data, optical filters and a photomultiplier combination were used as a photodetector to resolve the spectral shape. But the resolution of the optical filters is low (bandwidth $<$10 nm), so it was impossible to determine peak positions accurately. In addition, the Si sample was placed in the air during measurements. The spectrum of Si was affected to some extent by luminescence from the native oxide on Si, the molecules excited in air, bremsstrahlung produced by fast electrons, and atmosphere contamination effects.

In the present work, an apparatus was designed specifically for an accurate determination of the emission spectrum from Si in the visible–ultraviolet region, and much improvement has been made in the experimental conditions. In order to obtain high-quality CL spectra from Si, single-crystal Si wafers, cleaned to remove native oxides, were mounted in a vacuum chamber, and excited with a collimated low-energy ($<$10 KeV) electron beam, the energy of which is much lower than that of the fast electrons (MeV) from a ^{90}Sr β source. In this case, CL spectra for Si did not suffer from the effects of air and bremsstrahlung. The effect of the native

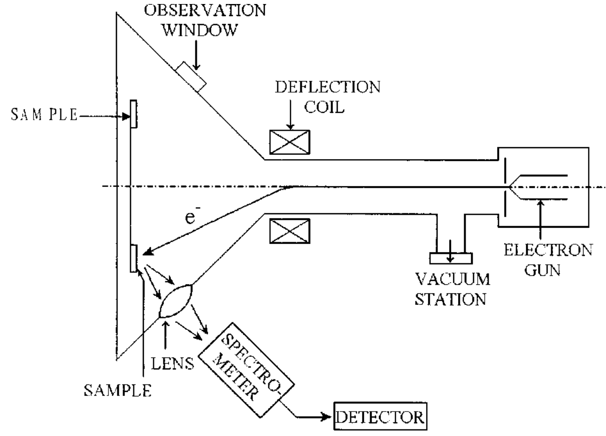

FIG. 1. Schematic drawing of the apparatus used to obtain the cathodoluminescence spectra of Si and SiO_2 films.

oxide was also decreased. The weak luminescence of Si was recorded with a suitable spectrophotometer for better resolution and an efficient photodetector. The goals of this paper are to verify further the existence of the luminescence for Si above the absorption edge (approximately 1.1 μm) under improved conditions, to determine the positions of peaks accurately, and then to compare them with optical structures in the literature, and attempt to attribute some emission peaks to particular direct-interband transitions.

II. EXPERIMENT

The apparatus used to obtained the cathodoluminescence spectra is shown schematically in Fig. 1. The vacuum system consists of an oil diffusion pump and a mechanical forepump. The base pressure of the vacuum chamber is 3×10^{-6} Torr. A liquid-nitrogen trap was used to reduce oil vapor from the diffusion pump. In this way, carbon contamination on the sample due to the electron beam was reduced. The electron gun was operated in the grounded anode configuration. The radiation power of the electron beam was carefully selected. On the one hand, the power should be large in order to keep the emission intensity at reasonable levels in comparison to the system noise; on the other hand, low power is required to minimize the radiation-induced damage. Usually a beam current between 0.03 and 0.1 μA at 3–10 kV was used. The beam could be deflected vertically and horizontally using a pair of deflection coils, and was slightly defocused. The sample was impacted by the broad beam, so that a luminous spot of approximately 3 mm in diameter was generated on the sample. The light spot thus produced was focused through a quartz collective lens onto the entrance slit of a monochromator. A XP2020Q photomultiplier tube (PMT), operated in the single photon-counting mode, detected the radiation at the exit of the monochromator. After amplification, the PMT signal was fed into a counting device. During measurements, the beam current was held constant. All measurements for this experiment were carried out in a dark room, the temperature of which was maintained at 14 °C. The resolution of the entire optical system is 2 nm in the wavelength range 250–600 nm.

The samples used in this study are two different kinds of single-crystal silicon, 0.05-Ω cm P^+-type ⟨111⟩, 0.013-Ω cm N^+-type ⟨100⟩, and a SiO_2 film, 500 nm thick, grown thermally on a 3–10-Ω cm N-type silicon substrate. The moderately doped Si samples, whose resistances are low, were chosen to reduce the obstruction of the space charge which sets limits to the attainable electron currents. By covering the SiO_2 film with a copper net, one can recover the charge leaked from it. Three samples, approximately $11\times15\ \mathrm{mm}^2$ and about 1 mm thick, could be mounted at a time. The samples were placed off axis to prevent light from the filament from being reflected into the monochromator. Since the surface condition of the Si is the critical part of the CL experiment, special care was taken in the preparation of the sample surfaces. Before the samples were mounted in the holder, they were first optically polished and etched in HF (>40% concentration) for 10 min for Si, 2 s for SiO_2, immediately followed by washing in ethyl alcohol and deionized water followed by hot air drying. Samples were subsequently handled with clean tweezers. This cleaning procedure should remove the native oxide on Si completely and produces surfaces of Si and SiO_2 film with minimum contaminations.[26,27] After etching, the silicon wafers were exposed to air for a minimum of time (<5 min) necessary for mounting in the vacuum chamber. This procedure gives Si with native oxide surface layers of less than 1 nm thick.[28,29]

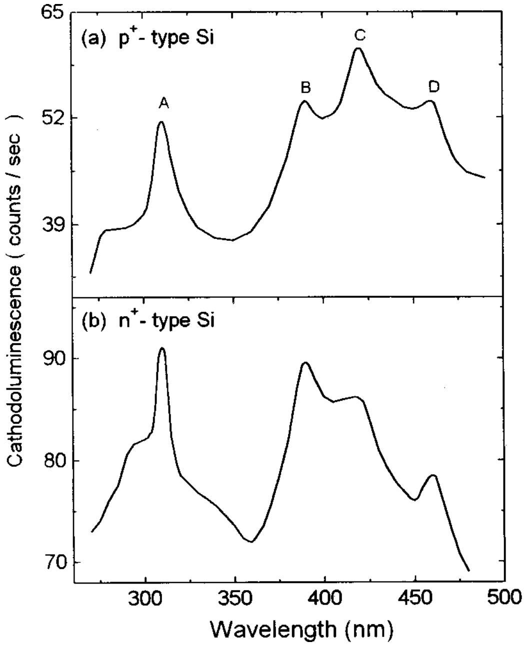

FIG. 2. Cathodoluminescence spectra of N^+- and P^+-type Si bombarded with a 4-keV, 0.05-μA electron beam: (a) N^+-type Si; (b) P^+-type Si.

III. RESULTS AND DISCUSSION

Figure 2 shows CL spectra for two different kinds of single-crystal silicon, P^+ type and N^+ type, uncorrected for the system response. The bombarding electron-beam voltage is 4 keV, and the beam current is 0.05 μA. It is clear from Fig. 2 that the emission spectral shape of the n- and p-type samples are similar. There are four peaks, labeled A at ~310 nm, B at ~390 nm, C at ~420 nm, and D at ~460 nm. In both Si samples, we have also measured the dependence of

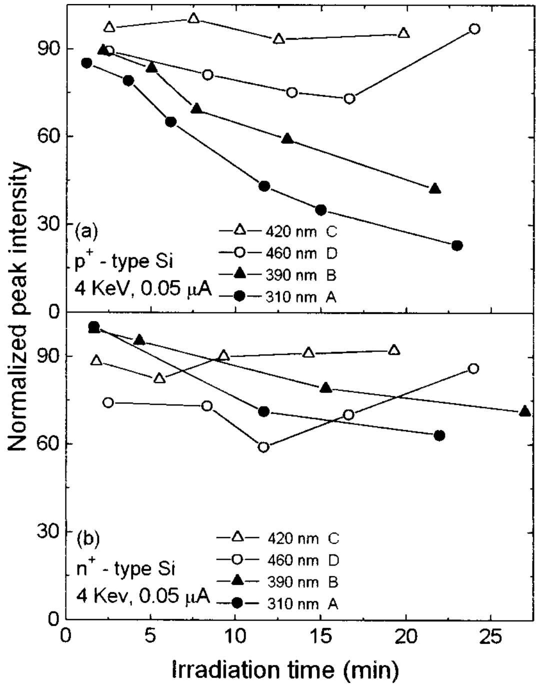

FIG. 3. Dependence of the peak intensity as a function of irradiation time for N^+-type Si and P^+-type Si: (a) intensity vs time for N^+-type Si; (b) intensity vs time for P^+-type Si.

the CL intensity on time. The normalized peak intensities as a function of irradiation time are summarized in Fig. 3. It is evident that peaks *A* and *B* are substantially decreased by the electron irradiation, and *C* and *D* peaks appear to be little affected by the irradiation. To gain some insight into the effect of thin native oxide surface layers with thickness <1 nm, it is necessary to make a comparison between the CL spectra from Si and that from thermally grown SiO_2 on Si. In Fig. 4, we show the result of a SiO_2 film. In order to extract the intrinsic luminescence features, it is necessary to separate the extrinsic features of the Si spectrum.

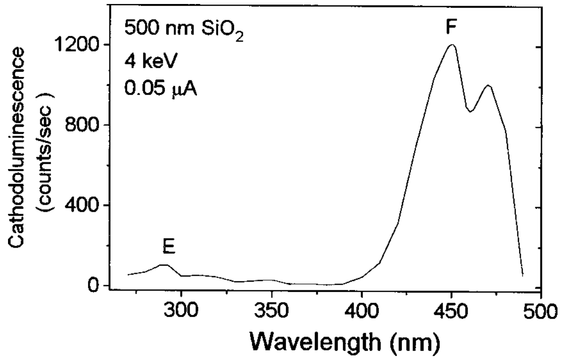

FIG. 4. Cathodoluminescence spectrum of a SiO_2 film on a Si substrate.

The observed emissions can be caused by several sources: the single-crystal Si itself, dopants in silicon, a native oxide surface layer on Si, and oil vapor from the diffusion pump. The Si samples are differentiated by dopant type and crystallographic orientation. But a comparison of Figs. 2(a) and 2(b) reveals a close similarity between the two emission spectra. This observation shows that dopant type and crystallographic orientation have little or no influence on the emission spectra. That is to say the four peaks observed are not related to dopant type and crystallographic orientation. On the other hand, when no liquid nitrogen trap was used, the CL *C* peak intensity at 420 nm increased, so that peak *B* was unresolved and peak *A* could not be determined. This observation indicates that peak *C* is associated with oil vapor from a diffusion pump. As shown in Fig. 3, the intensity of the *C* peak does not fall with electron irradiation. Studies done by others[30] showed that (1) oil vapor from a diffusion pump forms carbon contamination at the surface of the samples as a result of electron bombardment, and such carbon contamination exhibits a CL emission peak at 415 nm; (2) because this peak is related to implanted carbon rather than structural changes induced by the electron irradiation, the intensity of the peak saturates from the beginning of the irradiation. This behavior is similar to the time dependence of the intensity of peak *C* depicted in Fig. 3. Their results are the same as ours. Therefore, we conclude that the oil vapor from the diffusion pump is responsible for the *C* peak at 420 nm. Our measured CL spectrum of SiO_2 film shows two peaks (seeing Fig. 4), one located at 290 nm and 450 nm, labeled *E* and *F*, respectively. The main features are similar to those previously published.[31–34] The origin of the splitting of the 450-nm band is currently unknown. This splitting has been noted previously by Skuja.[35] A comparison of Figs. 2 and 4 shows that the agreement in wavelength position of peaks *D* and *F* is good. There are arguments about the origin of the peak *F*,[26–29] which may be a trivalent Si, a twofold-coordinated Si, self-trapped exciton, or something else, but the time-dependence measurements of the luminescence are similar,[31,35] and similar to that found for the Si samples of Fig. 3: the *D* peak intensity does not decrease from the irradiation. These suggest that peaks *D* and *F* are related to a common emission observed in SiO_2, i.e., peak *D* is an intrinsic emission of the native oxide surface layer on Si. The difference observed between the intensity of peak *D* and that of peak *F* results from the fact that the thickness of the SiO_2 film is considerably larger than that of the native oxide on Si. Mitchell[31] *et al.* showed that the CL intensity of this emission decreases with oxide thickness. The discrepancy in the exact peak position is due to differences in the samples. Although the *F* peak is common to all types of SiO_2, its peak position, which is correlated with the manufacturing processes of samples, may vary from 440 to 470 nm.[29,31,35–37] From the above discussion, it is apparent that the other sources, except Si itself, do not produce *A* and *B* peaks. Referring to Fig. 3, the difference of the time dependence of intensity between peaks (*A*,*B*) and peaks (*C*,*D*) also suggests that origin of the *C* and *D* peaks are different from that of the *A* and *B* peaks. On the basis of the evidence discussed above, we undoubtedly conclude that the peaks *A* and *B* are intrinsic to single-crystal silicon. The decrease of peaks *A* and *B* arises from radiation damage. The two peaks are new visible UV emission of Si, and their positions are determined accurately.

Experimental and theoretical investigations of reflectivity and photoemission spectra have revealed some direct-interband transitions which produce an obvious optical structure, and their identifications, including the location in the Brillouin zone, energy (eV), and symmetry for Si.[38–41] But, for two reasons, we cannot make peaks *A* and *B* correspond

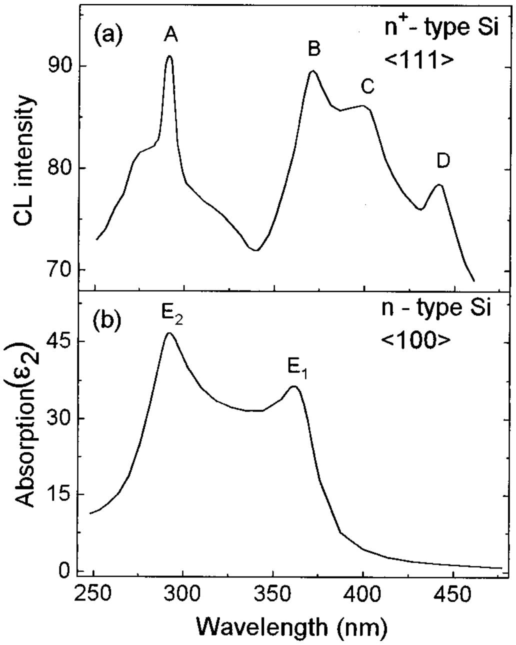

FIG. 5. Comparison of (a) absorption of Ref. 44 and (b) our CL spectra for Si. The CL spectrum is shifted ~0.2 eV to higher energy relative to the experimental one, thus facilitating spectral shape comparison.

to the special interband transitions previously reported in the literature only according to transition energies—peak energies. The first reason is that there exist peak shifts between absorption and emission spectra. The second is that considerable uncertainty remains in the intrinsic values of the interband transitions of Si in the visible–ultraviolet spectral range.[39–45] As an example, for a transition such as that $L_{3'}$-L_1, the following energy differences have been reported: 3.25 eV by reflectivity measurement,[42] 3.7 eV by photoemission,[43] 3.4 eV by reflectivity[44] and electroreflectance,[41] and 2.56 and 3.49 eV by calculation.[39,43] All differences in the reported transition energy result from the use of different measurement techniques and analysis, especially the temperature dependence of the optical absorption. To compare the optical properties with the band structure, one must express the transitions in terms of the complex dielectric constant $\varepsilon=\varepsilon_1+i\varepsilon_2$. $\varepsilon_2=2nk$ (n is the refraction and k the extinction coefficient) is the fundamental optical parameter, which is proportional to the optical absorption. Under present experimental conditions, we have obtained Si CL spectra which are sufficiently precise for direct comparison to ε_2 spectra recorded from high-precision scanning ellipsometry.[41,44] It is interesting to note that both CL spectra and the ε_2 spectrum, also known as the optical-absorption spectrum, of Si show two prominent peaks [see Fig. 5(a)]. The two peaks in the ε_2 spectrum,[46] labeled E_1 and E_2 are a general feature of IV, III-V, II-VI semiconductors.[47,48] The E_1 and E_2 features move monotonically to lower energies as the temperature is increased,[49] so that here we are concerned only with the E_1 and E_2 values at room temperature, in order to compare them with our room-temperature CL spectra. Numerous room-temperature measurements[38,41,44,49,50] have reported $E_1\sim3.4$ eV, and $E_2\sim4.25$ eV. As shown in Fig. 2, the CL peaks occur at 4.0 eV (peak A, 310 nm) and 3.2 eV (peak B, 390 nm). If we were to increase the CL peaks slightly by ~0.2 eV, the resulting positions of two CL peaks would be in accord with those of E_1 and E_2, respectively. In addition, as can be seen by comparing Figs. 5(a) and 5(b), the spectral shapes of CL and ε_2 are similar in the 250–400-nm spectral range. Therefore, we can consider that E_1 and peak B, and E_2 and peak A, arise from same transitions, respectively. The evidence for this reasoning is reinforced by the following explanations. As Kirchhoff's law states,[51] there is a general relationship between the radiation from a body in a small spectral interval and the absorption of the body in the same interval. The reciprocals of all the absorption processes lead to emission; for example, the excitation spectrum of photoluminescence. The fact that the CL peaks are about 0.2 eV below the corresponding absorption peaks is characteristic of a redshift. That is, the emission shift to the long-wavelength side of the absorption band. The redshift phenomenon is a general characteristic of condensed matter.[52–56] The most typical cause of such a shift is interband[57] and intraband[58] energy transfer, and the self-absorption of the light emission.[59] Reflective and photoemissive studies[19,46,60–62] have established the identity of the transitions giving rise to E_1 and E_2 structures: E_1 stands for electronic transitions across nearly parallel bands at L or along the Λ ($L\Gamma$) direction and E_2 for transitions in a large neighborhood of the X point in the Brillouin zone. The modulated reflectivity[17,40,63,64] study gives same assignment for E_1, but reveals that the contributions to E_2 are associated with the transitions not only around X but also along Σ. This shows that peaks A and B are due to emission from the parallel bands at $L(L_{3'}-L_1)$ or along $\Lambda(\Lambda_3-\Lambda_1)$, around $X(X_4-X_1)$ and along $\Sigma(\Sigma_2-\Sigma_3)$, respectively.

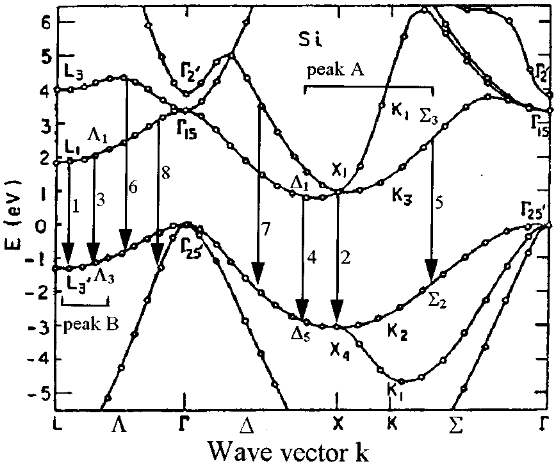

FIG. 6. Band structure of Si with competing direct electron transitions indicated at symmetry points (1 and 2), along $E(k)$ ranges with parallel bands and comparatively high joint densities of states (3, 4, and 5), transitions from higher conduction bands (6 and 7), and transitions into the light-hole valence band (8).

Further support for the assignment comes from the theoretical analysis. Most intrinsic transitions are direct transitions, which can proceed from any point in k-space with the appropriate photon energy[65(a)] (referring to Fig. 6), so a general smooth emission spectrum occurs. According to Fermi's golden rule, the luminescence intensity is proportional to the square of transition matrix elements and the joint density of states.[23,65(b)] Because the matrix element varies little within the Brillouin zone,[65(c)] it can be neglected in a qualitative analysis of the peak placement.[39,66] This means that the emission spectrum peaks around the ranges where the joint density of states has a maximum. These ranges in $E(k)$ are called critical points (Van Hove singularities) of a joint density of states, where both bands involved in the transition run parallel to each other for an extended k range. Critical points appear at or near high-symmetry points and along the symmetry axis of the Brullouin zone. Only two sets of critical points—the first at L and along Λ, the second along the Σ and Δ axes near the X point—should be considered, because the critical points of these symmetry points may contribute to the E_1 and E_2 structures, respectively, as a result of the energy-band-structure calculations.[67–71] Based on theoretical and experimental studies, various authors.[38,40,41,63,64,72,73] have suggested that the first set of critical points are of M_0 or M_1 singularity, the second M_1 or M_2. We think these critical point features will appear in the experimental CL spectra; they are simply peaks A and B. Although other critical points may be possible, they are not practical as compared with that mentioned above. For clarity, the transitions associated with peaks A and B are shown in Fig. 6. They are labeled according to the standard convention. The assignment, however, may be tentative because it depends largely on the results of the existing energy band-structure calculation.[67–71] It is hoped that our CL data will stimulate more accurate model calculations, which can provide insight into these spectra.

IV. CONCLUSIONS

The present work has obtained demonstrably accurate CL spectra from Si in the visible–ultraviolet region, then determined the peak positions accurately. A high correlation between CL and ε_2 spectra reveals that the CL is the reciprocal of the light absorption Also, the CL spectrum of Si is redshifted by about 0.2 eV against its absorption spectrum. Peak B near 390 nm, corresponding to the E_1 structure in ε_2, arises from the transitions at L or along the Λ direction. Peak A near 310 nm, which correlates well with the E_2 structure of ε_2, is due to transitions around X and along Σ.

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