Recombination Luminescence in N-type Czochralski Silicon*

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Radiative recombination of optically injected electron-hole pairs has been observed in Co^{60} gamma ray- and neutron-irradiated n-type Czochralski silicon. At liquid nitrogen temperature, two bands, peaking at 1.31 microns and 1.66 microns, are seen in gamma ray irradiated material. Neutron irradiated material differs in that the long wavelength band in the 1.6 micron region is simply a long wavelength tail. At liquid helium temperature, two complex luminescence patterns are seen in both neutron and gamma irradiated material. Intense bands appear at 0.969 eV and 0.789 eV with much of the structure replicated with a separation of 0.180 eV. It is suggested that the luminescence is due to recombination between free holes and electrons in the ground states of two different defects, 0.196 eV and 0.376 eV below the conduction band minimum, the weaker bands of the two patterns arising from recombination accompanied by phonon emission.

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I. INTRODUCTION

In recent years, there has been intensive research on the problem of determining the nature of radiation induced defects in silicon. Electron spin resonance has been particularly successful in providing detailed microscopic models of many of the prominent defects. Measurements of the transport properties of free carriers, either optically or thermally excited, and optical absorption have been successfully used to locate the energy level in the forbidden gap associated with the defect. Although recombination luminescence studies have been made on impurity defects introduced during crystal growth,[1-4] this technique has been used very little to study the properties of radiation induced defects.[5-8]

Ivanov and Yukhnevich[5,6] studied the recombination luminescence resulting from electron-hole recombination in Co^{60} irradiated silicon. The carriers were electrically injected into p-n junctions. Yukhnevich suggested that the luminescence resulted from the recombination of an electron-hole pair bound at the Si-A center, a defect consisting of a substitutional oxygen impurity having an energy level about 0.17 eV below the conduction band. It was suggested that phonon assisted transitions also occurred.

The present work was undertaken with the view of comparing the nature of the luminescence introduced by both Co^{60} and fast neutron irradiations, and to determine the influence of the nature and amount of dopant, both intentionally added impurities and accidental impurities, such as oxygen, upon the luminescence spectra, and to extend the temperature range of measurements to lower temperatures where thermal effects

[redacted]

would become less important. The results of a portion of these measurements, specifically those on Czochralski grown n-type material, are presented below.

II. EXPERIMENTAL PROCEDURE

All samples were phosphorus doped and grown by the Czochralski method, thereby containing about $10^{18}/cm^3$ interstitial oxygen atoms.[9] The samples were cut in the form of plates whose thickness ranged between 0.4 mm and 0.9 mm after etching in CP4A ($5HNO_3$, 3HF). About 0.08 mm of material was removed from each side after about one minute in the etch, leaving a surface which had an over-all "orange peel" appearance but which was smooth over distances comparable to the wavelength of the emitted light. After the etching action was quenched by flushing with distilled water, the samples were dried on filter paper and immediately placed in a vacuum dewar. Although the absolute luminescent efficiency was found to depend rather critically upon the etching procedure, no change in the luminescent spectrum was found to result from various surface treatments.

Electron-hole pairs were created by focusing a 500 watt high pressure mercury lamp on the sample. Photons with wavelengths greater than 7500 Å were removed by passing the incident light beam through a 5 cm water cell whose ends were made of Jena KG3 optical glass 3 mm thick. The incident exciting light was interrupted by a mechanical chopper. This excitation technique is similar to that used by Haynes.[10] The emitted light was collected from the side opposite the incident beam by a CaF_2

lense, analyzed by a monochromator, and detected by a PbS cell cooled to dry ice temperature. The voltage signal from the detector was amplified by a preamplifier and a Princeton Applied Research amplifier whose reference signal was generated by the mechanical chopper. The final signal was displayed on a chart recorder. Data were obtained continuously as a function of wavelength at liquid helium and liquid nitrogen temperature with a Jarrell-Ash model 82-092 grating monochromator. Many of the liquid nitrogen temperature measurements and higher temperature experiments were made with a Perkin Elmer Model 83 prism monochromator. The relative response of the detector and monochromators was determined by a measurement of a blackbody source operating at a known temperature. All data are presented in terms of the relative number of quanta emitted in a given wavelength interval.

The samples were irradiated at room temperature by gamma rays from Co^{60} and by fast neutrons from a General Dynamics Triga reactor. Thermal neutrons were removed by shielding the samples with a cadmium foil 0.030 inches thick. The samples were re-etched for about 10 seconds after each irradiation.

III. RESULTS

A. Liquid Nitrogen Temperature

The luminescence spectrum at liquid nitrogen temperature of Co^{60} gamma ray bombarded silicon of 100 ohm resistivity is shown in Fig. 1. The band-to-band luminescence at 1.13 microns was first reported by Haynes and Westphal.[11] The lower resolution used in the present measurement produced the greater half width in this band than that reported by these workers. As the integrated gamma flux increases, the band gap luminescence disappears, leaving two new bands peaking at 1.31 microns and 1.66 microns corresponding to 0.947 eV and 0.747 eV respectively. The spectrum for neutron bombarded material shown in Fig. 2 differs in that the distinct second band now appears simply as a long wavelength tail. The slight variation in the location of the peak of the intense band is due to a difference in the instrumental resolution used in the two measurements. Neither the long wavelength band nor tail were observed in similar studies of float zone grown silicon. All the spectra disappeared at dry ice temperature.

These results are in general agreement with those of Ivanov and Yukhnevich,[5] who found two distinct bands at liquid nitrogen temperature which appear to be identical to those in Fig. 1. They found that the luminescence disappears at 120°K. In a subsequent study,[6] Yukhnevich was able to observe structure on the 1.31 micron band; in particular he reports an intense band at 0.967 eV that has a measured half width of less than 0.002 eV. By going to an instrumental resolution of 0.0024 eV, we also observed this line but found the half width to be 0.0050 eV. There remains an unexplained discrepancy in the measured half width of this band as reported by Yukhnevich and as found in the present work.

Yukhnevich has also observed a complex emission spectrum[8] in the 2.4 micron to 3.0 micron range which we have not observed.

B. Liquid Helium Temperature

The results for gamma irradiated silicon at liquid helium temperature are shown in Fig. 3. It is particularly striking that two similar complex patterns appear which are displaced by 0.180 eV. The bands located at 0.717 eV, 0.773 eV, and 0.789 eV appear to be uniformly replicated at 0.898 eV, 0.953 eV, and 0.969 eV respectively. In addition to the clear replication of these three luminescent bands, there is an indication that the small peaks at 0.755 eV and 0.739 eV are also replicated at 0.935 eV and 0.919 eV respectively. There are dissimilar complex bands centered about 0.728 eV, 0.752 eV, and 0.923 eV. The spectrum between 0.64 eV and 0.80 eV was never observed in float zone grown silicon for which the oxygen content is about two orders of magnitude below that of the Czochralski grown crystals.

The two most intense bands of Fig. 3 were examined under the maximum resolution instrumentally available. The results shown in Fig. 4 indicate that the measured halfwidth is still instrumentally limited. It is clear, however, that the halfwidth of the 0.969 eV line decreases in going from liquid nitrogen to liquid helium temperature.

A comparison of the results obtained on the neutron and gamma ray irradiated silicon suggests that the principal features of the spectra are essentially the same. Thus, it can be concluded that the defects which are active as recombination centers in the silicon are essentially the same in both neutron and gamma ray irradiated material. It must be emphasized, of course, that the defects seen in the luminescence measurement may represent only a single type of a much larger group of defects produced by the radiation.

The fact that the halfwidth of the 0.967 eV line is of the order of kT at liquid nitrogen temperature and the fact that the halfwidth decreases when going to liquid helium temperature strongly suggest that the transition is due to recombination of a trapped carrier with a free carrier having a thermally broadened density of states. This is in disagreement with the conclusion of Yukhnevich[11] who attributed the transition to recombination of an electron and a hole both bound to an A center, after the model of Kurskii.[12,13] The great intensity of this band indicates that the transition proceeds without phonon cooperation.[3,4] It is suggested, therefore, that the recombination occurs between a free hole and an electron bound to a defect, the bound electron having an energy level near the conduction band. If the sharp line transition at 0.969 eV involves no phonons, the energy level would, therefore, be 0.196 eV from the conduction band edge. The other alternative would be for the defect itself to take part in the momentum transfer and to dissipate the momentum in a local mode vibration.

The value of 0.196 eV is larger than the depth of the A-center ground state,[14] as determined from transport measurements. Although it is possible that the transport experiments measure an ionization energy which may be less than the value seen here because of the cooperation of lattice vibrations in ejecting the electron, it is also possible that the defect responsible for the luminescence is not the A center.

It is suggested that the 0.953 eV band results from recombination with the accompanying emission of a transverse acoustic phonon. The 0.898 eV band corresponds to recombination with the emission of both a transverse acoustic and a transverse optical phonon.[15] The small bands present at 0.935 eV and 0.919 eV would correspond to emission with two and three transverse acoustical phonons, respectively. The origin of the 0.923 eV band is not known.

By similar arguments the 0.789 eV band is due to phononless recombination between a free hole and an electron trapped at a defect level 0.376 eV below the conduction band minimum. The 0.773 eV band is due to recombination with the emission of a transverse acoustic phonon and the 0.717 eV band is due to recombination with emission of both a transverse optical and a transverse acoustic phonon. By analogy with the above arguments, the bands at 0.755 eV and 0.739 eV may result from recombination with the accompanying emission of two and three transverse acoustic phonons, respectively. The origin of the 0.728 eV and 0.752 eV bands is unknown. Since the lower energy spectrum is found in only Czochralski material, the corresponding defect must depend upon oxygen for its formation but its exact nature is unknown. This model is supported by the data of Fan and Ramdas,[16] who measured the optical absorption and photoconductivity at 4.2°K of neutron and gamma irradiated n-type silicon. They found a strong absorption line at 0.343 eV and a series of weaker absorption bands located at higher energies, the two nearest bands being separated by 0.015 eV and 0.031 eV. The Fermi level had to be close to the conduction band to see the absorption and there was no photoconductivity associated with the center. If this center is the same as the one lying 0.376 eV below the conduction band, then the 0.343 eV absorption band is due to excitation of an electron into a state 0.033 eV below the conduction band and the two nearest absorption bands are due to single and double emission of transverse optical phonons.

In general, the luminescence spectrum appears to depend mainly on the local environment of the traps and upon the phonon spectrum of the crystal. It appears to be less sensitive to the exact structure of the defect. It seems clear that the techniques described in this paper are capable of yielding important information about the energy levels associated with the radiation induced defects and the interaction of these defects with the lattice phonons.

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FIGURE CAPTIONS

Fig. 1 Luminescence spectrum of 100 ohm-cm n-type Czochralski silicon at liquid nitrogen temperature. Irradiated with Co^{60} gamma rays. —— 1×10^6 Roentgens, resolution 0.04 microns. ---- 40×10^6 Roentgens, resolution 0.018 microns.

Fig. 2 Luminescence spectrum of 100 ohm-cm n-type Czochralski silicon at liquid nitrogen temperature. Irradiated with fast neutrons. —— $10^{12}/cm^2$. ---- $10^{14}/cm^2$. Resolution 0.04 microns.

Fig. 3 Luminescence spectrum of 100 ohm-cm n-type Czochralski silicon at liquid helium temperature. Irradiated with Co^{60} gamma flux to 10^8 Roentgens. Resolution 0.0064 microns.

Fig. 4 The intense luminescence peaks of Fig. 3, analyzed with a resolution of 0.0008 eV for the 0.7894 eV line and a resolution of 0.0012 eV for the 0.9688 eV line.

Fig. 5 Luminescence spectrum of 100 ohm-cm n-type Czochralski silicon at liquid helium temperature. Irradiated with fast neutrons to flux of $10^{14}/cm^2$. Resolution 0.0064 microns.

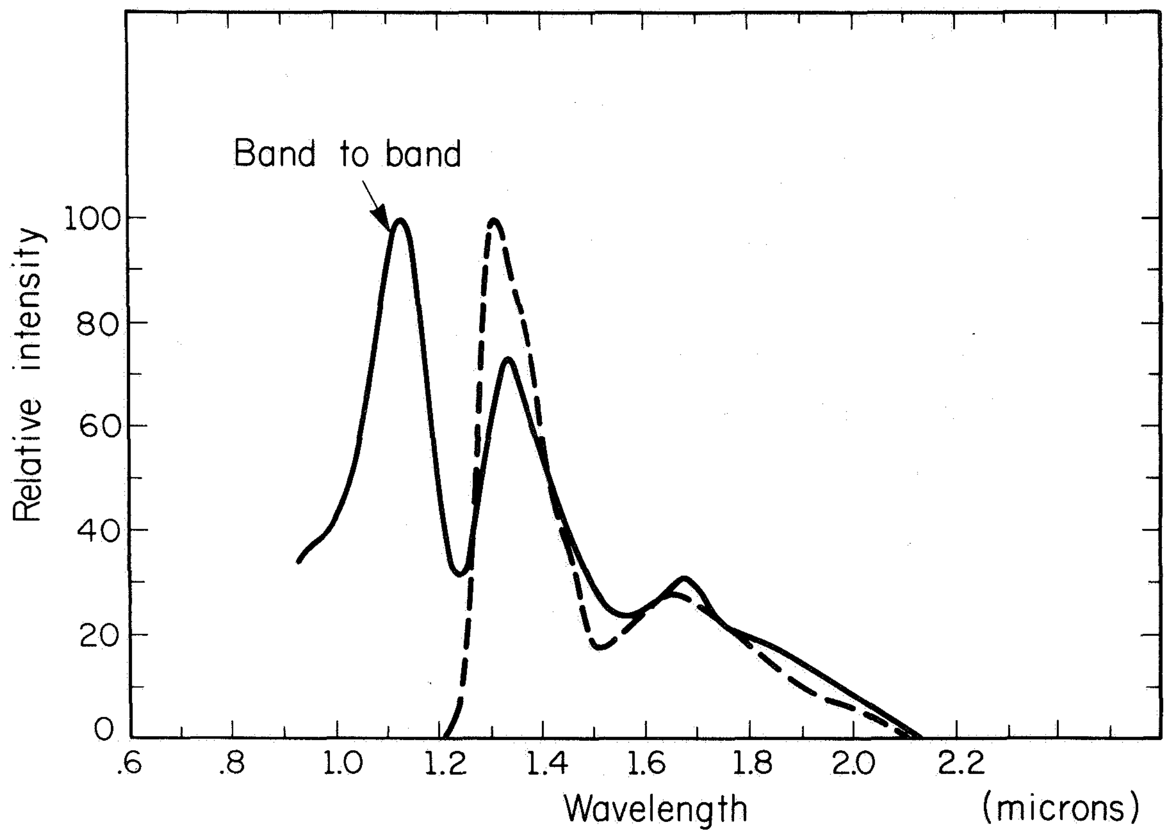

Band to band
Relative intensity
100
80
60
40
20
0
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
Wavelength
(microns)

FIGURE 1

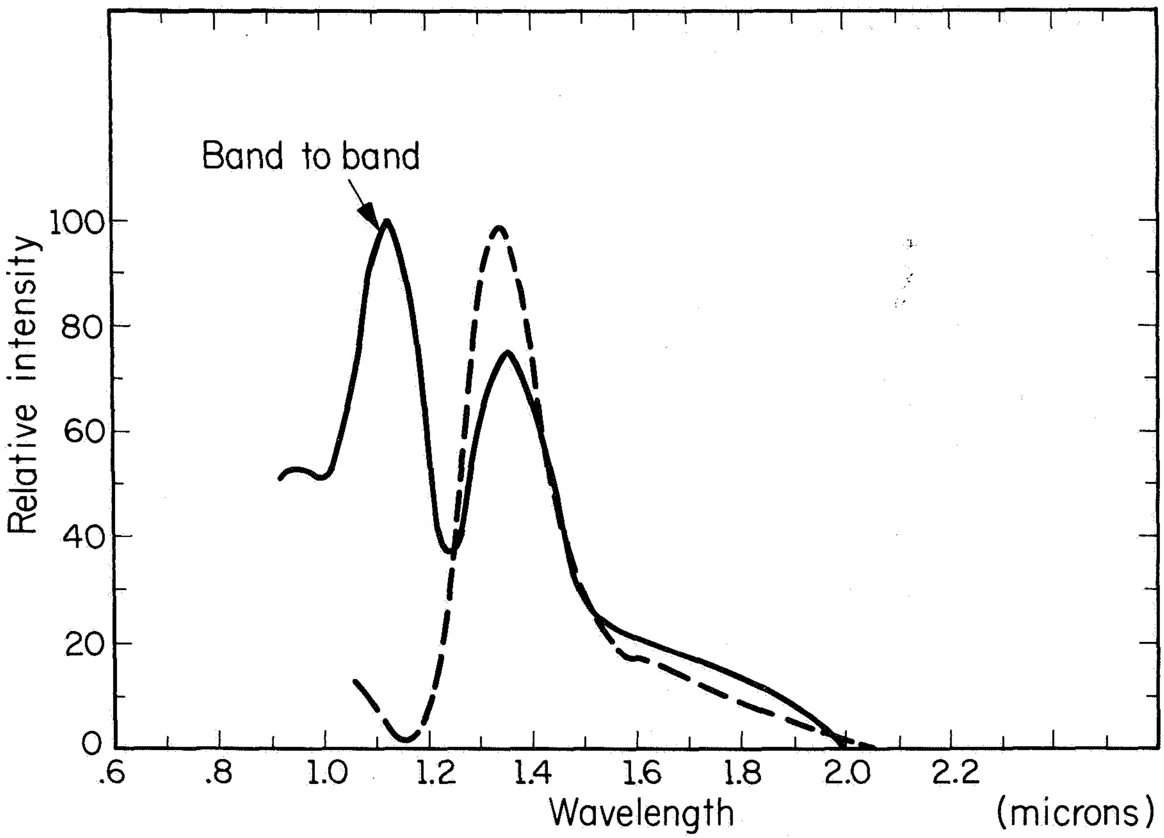
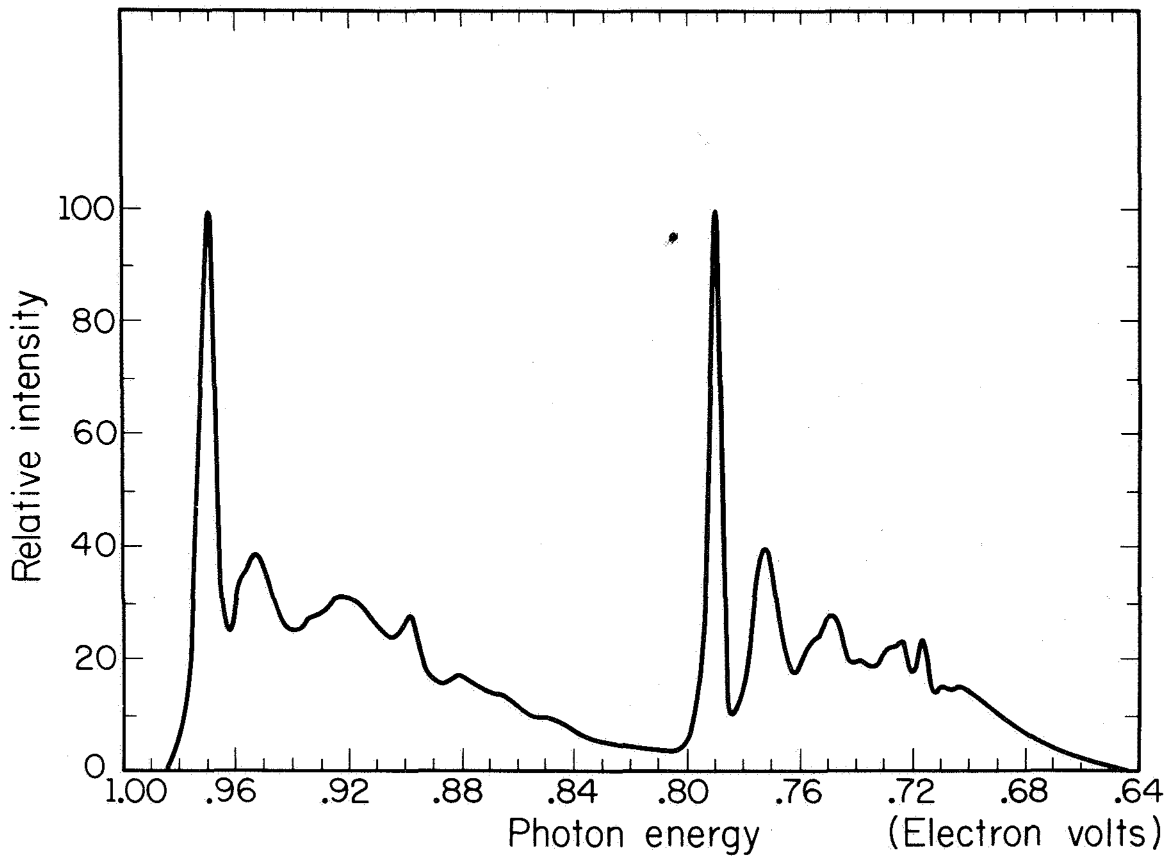

Band to band
Relative intensity
100
80
60
40
20
0
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
Wavelength
(microns)

FIGURE 2



100
80
60
40
20
0
Relative intensity
1.00
.96
.92
.88
.84
.80
.76
.72
.68
.64
Photon energy
(Electron volts)

FIGURE 3

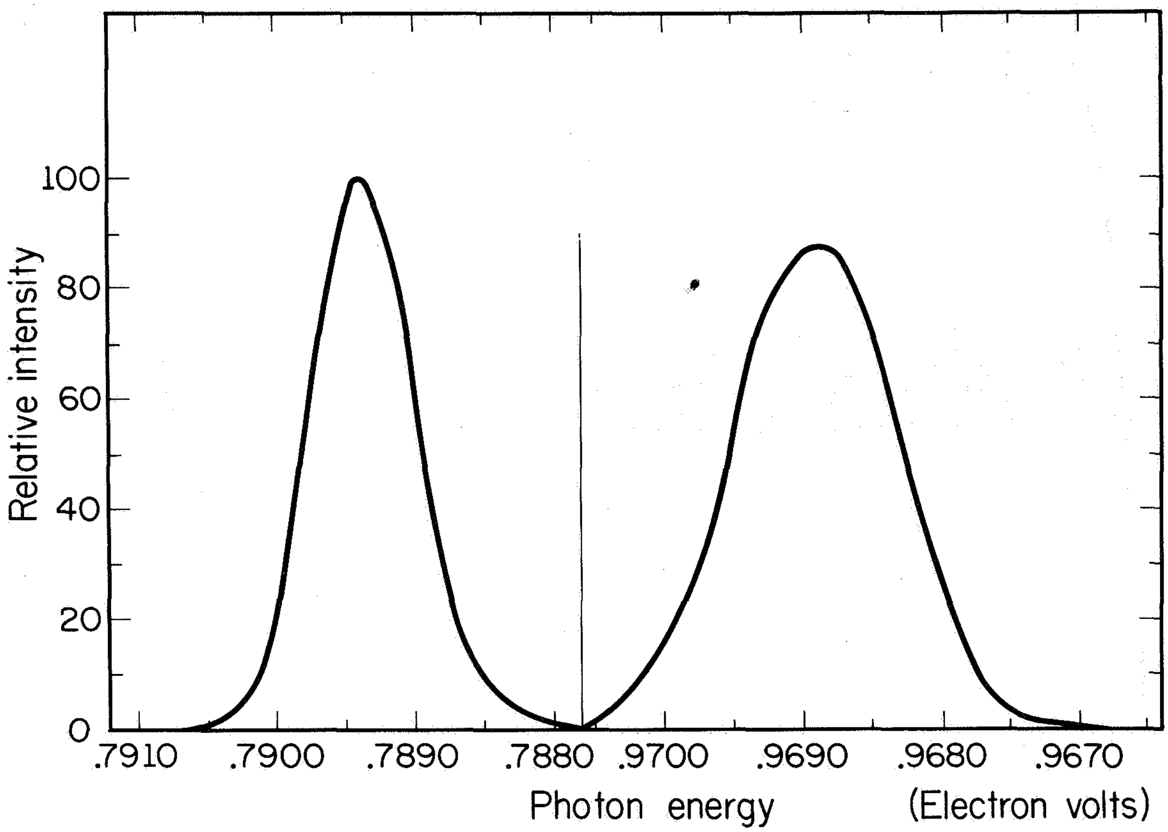
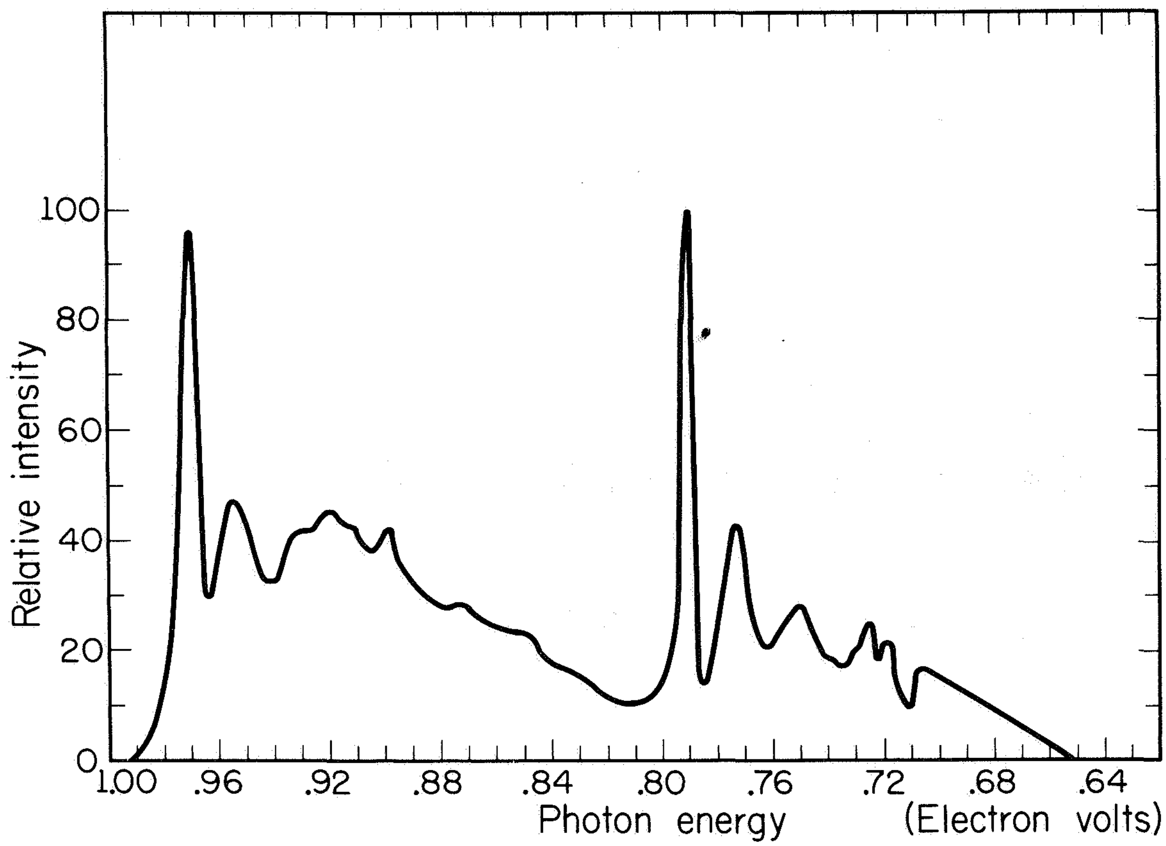

100
80
60
40
20
0
Relative intensity
.7910
.7900
.7890
.7880
.9700
.9690
.9680
.9670
Photon energy
(Electron volts)

FIGURE 4



Relative intensity
100
80
60
40
20
0
1.00
.96
.92
.88
.84
.80
.76
.72
.68
.64
Photon energy
(Electron volts)

FIGURE 5