Soft-X-Ray Electroreflectance: Final-State Effects on Si (2p) Optical Transitions (*).

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Summary. — Electric-field modulation techniques have been employed for the first time in the spectral region above 30 eV. A novel analog detection scheme is described which achieves sensitivities of 10^{-4} with the low-duty-cycle, pulsed synchrotron radiation source used. Application to the sharp Si $L_{2,3}$ edge at 99.9 eV yielded no detectable electroreflectance for $3\cdot10^5$ V/cm modulation. We conclude that the p-core exciton binding energy must be at least 300 meV, and thus its final state cannot be described by the previously employed effective-mass approximation. Photoemission and absorption measurements are presented to support this finding.

1. – Introduction.

Modulation spectroscopy has proven to be an effective technique for enhancing weak optical transitions in the visible and in the near UV energy region [1]. The sharpness of the resulting structure and its dependence on the electric field have been successfully used to identify electronic energy band critical points

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([1]) See, for instance, M. CARDONA: *Modulation Spectroscopy* (New York, N. Y., 1969); see also papers in *Modulation Techniques*, edited by R. K. WILLARDSON and A. C. BEER, Vol. **9** (New York, N. Y., 1972).

and intrinsic bulk broadening energies (2). Similar measurements performed up to 27 eV by using synchrotron radiation exhibit surprisingly strong structural enhancement and high-resolution characteristics (3). Spectral features some five times sharper than expected on the basis of core level widths measured by photoemission and conventional absorption are seen.

We have extended the electroreflectance technique into the soft–X-ray region in order to measure transitions from a variety of core levels on all constituents of a semiconductor compound and to elucidate final-state interactions more clearly than in conventional optical experiments. In particular, in this paper we use the strength of the modulation response to characterize core exciton binding characteristics.

2. – Experiment.

While standard sample preparation techniques (4) can be used in the soft–X-ray region, novel signal processing has to be employed for an adequate signal-to-noise ratio to be realized, due to the pulsed nature of the synchrotron radiation source. Our experimental solution is outlined schematically in fig. 1.

Electrons circulating in the SPEAR storage ring at the Stanford Linear Accelerator Center emit 0.4 ns pulses of light every 781 ns, each having a continuum of photon energies extending into the hard–X-ray region. The monochromator on the 4° beam line (5) at SSRP provides tunable radiation from 30 to 500 eV with 0.1 Å resolution. The sample was placed at 5° grazing angle of incidence with the modulation region aligned in the light beam by maximizing the 68 eV, $M_{2,3}$ reflectivity structure of the semi-transparent Ni Schottky-barrier field electrode. The reflected intensity is detected by a chevron channel plate operated in an analog mode. Its pulsed response is characterized by the time structure of the electron stored in SPEAR, as shown at the top of fig. 1. Since the duty cycle is 0.05 %, the noise generated in the detector would be averaged for a period that is a thousand times longer than the time the optical signal is present, if standard analog techniques are used. We, therefore, achieve noise reduction by gating the detector output in synchronism with the pulse repetition rate of the storage ring for as short an interval as possible. In practice, a ≈ 20 ns window is achieved for each pulse with a PAR 162/164 boxcar

(2) V. Rehn: *Surf. Sci.*, **37**, 443 (1973); D. E. Aspnes: *Surf. Sci.*, **37**, 418 (1973), and cited references.

(3) D. E. Aspnes and C. G. Olson: *Phys. Rev. Lett.*, **33**, 1605 (1974).

(4) D. E. Aspnes: *Phys. Rev. Lett.*, **28**, 913 (1972).

(5) F. C. Brown, R. Z. Bachrach, S. B. M. Hagstrom, N. Lien and C. H. Pruett: in *Vacuum Ultraviolet Radiation Physics*, edited by L. Koch, R. Haensel and C. Kunz (New York, N. Y., 1975), p. 785.

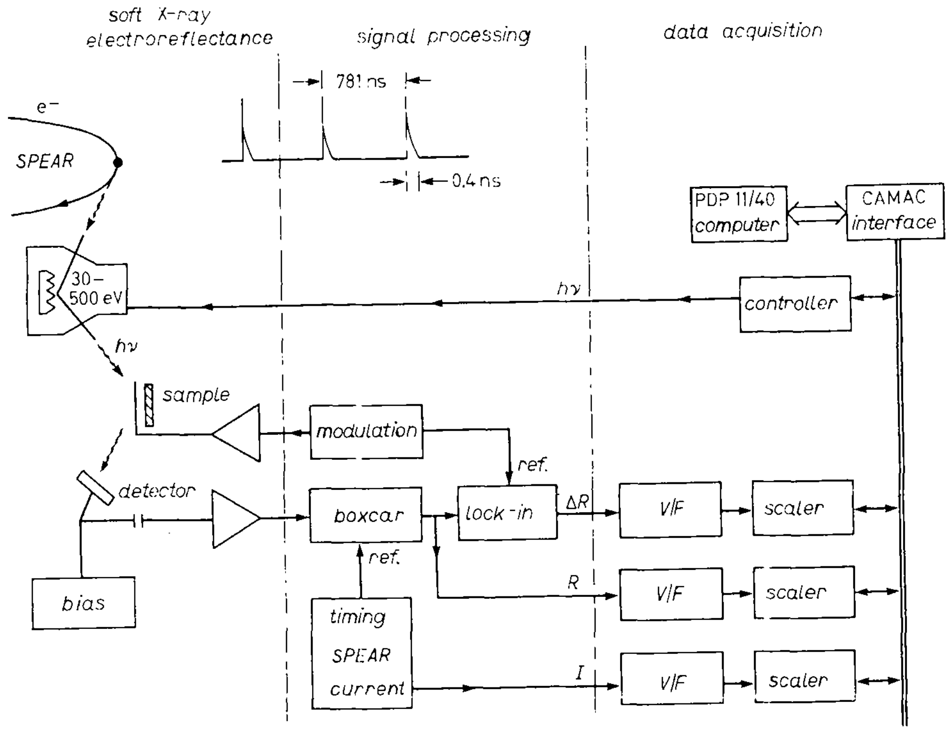

Fig. 1. – Schematic diagram of the apparatus used in this experiment. The monochromatized synchrotron radiation reflects at grazing incidence from the sample and is detected by a chevron channel plate detector working in an analog mode. The low-duty-cycle pulses are gated with a boxcar integrator. The slow electric-field modulated component is extracted with a lock-in amplifier. A computerized data acquisition system (6) encodes and reduces the raw data.

integrator operated in a sample-and-hold mode. This output can then be processed by usual modulation spectroscopy techniques. The boxcar output directly yields the reflectivity R following normalization by the SPEAR current I to account for the long-term decrease in photon flux as the stored electron beam decays. The electroreflectance response ΔR is obtained from the boxcar output by using a lock-in amplifier (PAR 124 A/116) operating at the fundamental or second harmonic of the modulation frequency. In our system, the processing required for a normalized $\Delta R/R$ was done by a PDP 11/40 computerized data acquisition system (6) by means of CAMAC modules and VIDAR voltage-to-frequency converters. A sensitivity of a few parts in 10^4 was routinely achieved.

(6) R. Z. Bachrach: *Proceedings of International Workshop on the Development of Synchrotron Radiation Facilities, Quebec City, June 1976.*

3. – Si $L_{2,3}$ electroreflectance.

The interaction between an excited core electron and the resulting localized core hole is fundamental to optical processes in the far UV. Because of its sharp ($\approx$ 0.12 eV) and strong threshold behavior [7,8], the silicon $L_{2,3}$ absorption edge at 99.9 eV has been the prototype for optical excitation of p core electrons. General theories of core excitons in semiconductors [9,10] estimate

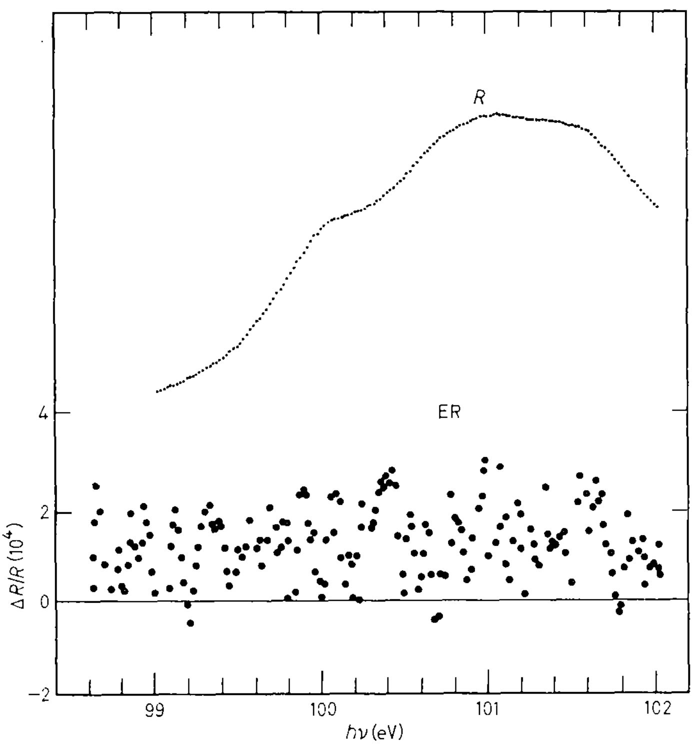

Fig. 2. – The raw spectral distribution of the grazing-incidence reflectivity R for Si in the region of the $L_{2,3}$ edge at 77 K. The lower data are the simultaneously measured electroreflectance ER ($\mathscr{E}_s = 3\cdot10^5$ V/cm) signals; the depletion region modulation in this sample was excellent, as measured by ER in the visible region.

(7) R. Z. BACHRACH, F. C. BROWN and M. SKIBOWSKI: *Bull. Amer. Phys. Soc.*, **20**, 488 (1975); F. C. BROWN, R. Z. BACHRACH and M. SKIBOWSKI: *Phys. Rev. B* (to be published).

(8) F. C. BROWN and O. P. RUSTGI: *Phys. Rev. Lett.*, **28**, 497 (1972); C. GAHWILLER and F. C. BROWN: *Phys. Rev. B*, **2**, 1918 (1970).

(9) M. ALTARELLI and D. S. DEXTER: *Phys. Rev. Lett.*, **29**, 1100 (1972).

(10) S. T. PANTELIDES: *Sol. State Comm.*, **16**, 217 (1975).

the binding energy for the Si $L_{2,3}$ excitonic final state to be of the order of 40 meV. We have applied modulation techniques to this transition for the first time in order to characterize core exciton binding characteristics.

Using the techniques described above, we measured electroreflectance of Si at 5° angle of incidence in the region of the $L_{2,3}$ edge at 77 K. As seen in the top of fig. 2, the unmodulated grazing-incidence reflectance spectrum obtained for these samples is better resolved than those previously reported ([11]). A strong $M_{2,3}$ Ni structure is obtained at 68 eV, indicating good alignment of the modulation region in the light path. The data in the lower part of the figure show that for fields of $3 \cdot 10^5$ V/cm, no electroreflectance is measured to a few parts in 10^4, even though a strong structure is clearly observed in the normal reflectance. This particular Si sample was measured in the quartz-optics range before and after the soft–X-ray experiments were performed; the low-energy electroreflectance was among the strongest ever measured for Si, indicating that good depletion region modulation had been achieved in the experiments in fig. 2.

The Si $L_{2,3}$ electroreflectance should have been easily observable with our experimental capabilities, if the final state for the photoexcited $2p$ core electron were effective-mass–like ([9,10]). By comparing the results for Ga ($3d$) electroreflectance in GaP ([3]), a 170 meV exciton binding energy for the Si $2p$ final state would have yielded a signal that is a factor of two greater than the noise shown in fig. 2; this value was calculated by using Blossey's theory ([12]) with an electro-optic energy of 57 meV for Si. A reasonable lower limit for the final-state effect to cause our null ER result is thus taken as 300 meV. Clearly, the excitation is too local to be understood by conventional effective-mass descriptions applicable to semiconductor donor states ([10]).

4. – Discussion.

This experimental finding is supported by photoemission and optical-absorption measurements. Electrons photoemitted by high-energy photons from both core and valence band initial states will not be influenced by excitonic effects for conduction band edge final states. We then can compare the edge position measured by optical absorption ([8]) with the core-to-valence band maximum (VBM) separation seen in photoemission. High-resolution photoelectron data for *in situ* cleaved Si are presented in fig. 3, as measured by a Physical Electronics 15-255 G double-pass cylindrical-mirror analyzer

([11]) H. FUJITA and Y. IGUCHI: *Jap. Journ. Appl. Phys.*, **14**, 220 (1975).
([12]) D. F. BLOSSEY: *Phys. Rev. B*, **2**, 3976 (1970); **3**, 1382 (1971); D. F. BLOSSEY and P. HANDLER: in *Semiconductors and Semimetals*, p. 257.

operating with an electron energy resolution of 0.4 eV (*i.e.* 25 V pass energy). Matrix element effects cause weak valence band emission at 150 eV (note the ×100 expansion) and the supression of *s*-derived density-of-state structure

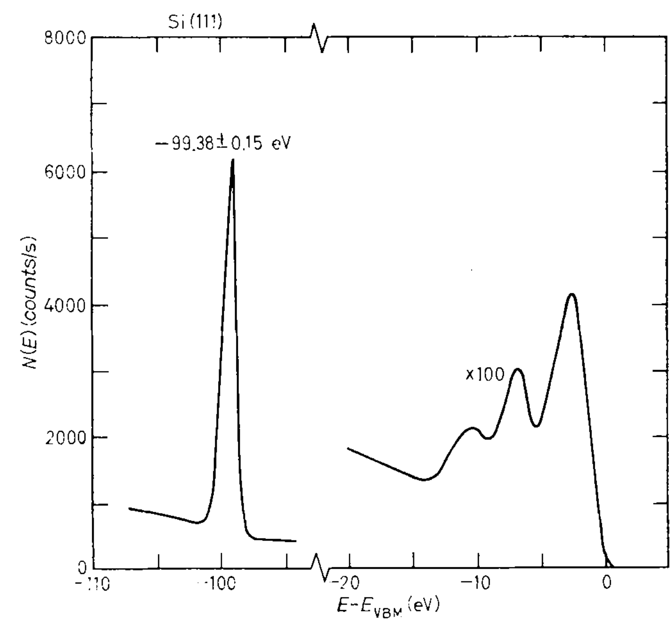

Fig. 3. – Initial-state energy distribution for electrons photoemitted from *in situ* cleaved Si for an excitation energy of 150 eV and at 300 K. By referencing to the valence band maximum (VBM), the one-electron continuum is determined.

seen at ESCA energies. Adding the 1.1 eV Si band gap energy to the 99.4 eV binding of the $2p$ core electron determined from fig. 3, the one-electron separation between this core and the conduction band edge is (100.5 ± 0.15) eV. Absorption experiments ([8]) measure (99.9 ± 0.05) eV as the optical-transition energy for this $L_{2,3}$ edge; this is in agreement with the absorption edges obtained by total ([13]) and partial ([14]) photoemission yield. Thus the final-state effect measured this way is of the order of (0.6 ± 0.2) eV. The minimum exciton binding energy then supports our deduction from the lack of electroreflectance.

Bachrach, Brown and Skibowski ([7]) studied the final state for Si $2p$ optical transitions by observing the effects of doping on the $L_{2,3}$ absorption edge. They showed that, while the edge is sensitive to local order in the vicinity

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([13]) W. Gudat and C. Kunz: *Phys. Rev. Lett.*, **29**, 169 (1972).
([14]) R. S. Bauer, R. Z. Bachrach, S. A. Flodstrom and J. C. McMenamin: *Journ. Vac. Sci. Technol.*, **14**, 378 (1977).

of an absorbing Si atom, no changes in line shape or position occur when Si is doped metallic with 10^{20} donors per cm^3. Therefore, this soft–X-ray transition must be more local than the ≈ 20 Å screening length in those samples.

5. – Conclusion.

The photoexcitation of a deep p-core electron must be relatively local, and, therefore, one-electron band states cannot constitute the final states for these transitions ([7]). Theories based on stronger interactions than possible in the effective-mass approximation ([9,10]) are necessary to describe these core excitons. We have accumulated photoemission and optical data on III-V and II-VI semiconductors which indicate that strong final-state effects on high-energy optical transitions are a general phenomenon, not limited to just the Si $L_{2,3}$ edge.

Our null result should not be taken as indicative of the general prospects for soft–X-ray electroreflectance data. Rather, the unique ability to study the response of a large variety of core level excitations to electric-field perturbation makes pursuit of this technique very promising at high photon energies. Our demonstration of adequate signal-to-noise ratio above 30 eV should at least allow many of the generalizations based on studies of a single-core level (*viz.*, Ga 3d) ([3]) to be investigated.

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● RIASSUNTO (*)

Tecniche di modulazione di campo elettrico sono state impiegate, per la prima volta, nella regione spettrale al di sopra di 30 eV. Si descrive un nuovo sistema analogico di rivelazione che raggiunge sensibilità di 10^{-4} con la sorgente di radiazione di sincrotrone che è impulsata con basso « duty-cycle ». La tecnica è stata applicata alla stretta soglia di assorbimento $L_{2,3}$ del Si a 99.9 eV. Non si sono osservati segnali di elettriflettanza nonostante una modulazione di $3 \cdot 10^5$ V/cm. Si conclude che l'energia di legame dell'eccitone p profondo deve essere almeno 300 meV, e quindi il suo stato finale non può essere descritto dall'approssimazione della massa effettiva precedentemente impiegata. Si presentano misure di assorbimento e di fotoemissione a sostegno di questo risultato.

(*) *Traduzione a cura della Redazione.*

Техника электроотражения в области мягких рентгеновских лучей.
Влияние конечного состояния на оптические переходы Si(2*p*).

Резюме (*). -- Впервые техника модуляции электрического поля используется в спектральной области выше 30 эВ. Описывается схема детектирования, в которой достигается чувствительность 10^{-4}, когда используется импульсный синхротронный источник излучения. Применение к резкому краю Si $L_{2,3}$ при 99.9 эВ дает не детектируемое электроотражение для модуляции $3 \cdot 10^5$ В/см. Мы заключаем, что энергия связи для экситонов *p*-остова должна быть, по крайней мере, 300 мэВ. Таким образом, конечное состояние не может быть описано с помощью ранее использованного приближения эффективной массы. Приводятся результаты измерений по фотоэмиссии и поглощению.

(*) *Переведено редакцией.*