phys. stat. sol. (a) **113**, 503 (1989)

Subject classification: 71.55; S5.11

Solid State Section, Department of Physics, University of Athens[1]

Defect States in Electron-Bombarded n-Type Silicon

By

C. A. Londos

Deep level transient spectroscopy measurements on electron bombarded floating-zone n-Si Schottky diodes are reported. Activation energies and capture cross-sections of five observed majority-carrier traps ($E_c - 0.15$ eV, $E_c - 0.21$ eV, $E_c - 0.28$ eV, $E_c - 0.33$ eV, and $E_c - 0.45$ eV) are examined. Depth profiling and electric field effects on the thermal emission of the traps are also investigated. Identifications made by reference to the published literature are discussed.

Es werden DLTS-Messungen an elektronenbestrahlten Schottkydioden aus n-leitendem zonengezogenem Si durchgeführt. Aktivierungsenergien und Einfangsquerschnitte von fünf beobachteten Majoritätsträgerhaftstellen ($E_c - 0{,}15$ eV, $E_c - 0{,}21$ eV, $E_c - 0{,}28$ eV, $E_c - 0{,}33$ eV und $E_c - 0{,}45$ eV) werden untersucht. Tiefenprofil und Einflüsse des elektrischen Feldes auf die thermische Emission der Haftstellen werden ebenfalls untersucht. Die Identifizierung anhand der Literaturdaten wird diskutiert.

1. Introduction

The knowledge of the nature and the properties of defects with electrical active states within the forbidden gap of semiconductors is of paramount importance for the electronic technology. Especially for the widely used Si material the improvement of the device performances requires a profound understanding of every available information concerning defect states. Each particular defect may be related with a particular characteristic of the behaviour of the material. Therefore, manipulating the properties of defects we could control the yield and performance of the devices.

The concentration of defects arising accidentally in the crystals during their growth and processing are often too small to allow proper investigation. One of the most efficient methods to introduce these defects in higher concentrations is irradiation with high-energy electrons. The scope of this communication is to present the result of electron-irradiation-induced defects studies in the upper half band gap of high-purity n-Si.

2. Experimental

Wafers of (111) orientation of phosphorus-doped ($\varrho = 100$ to $120\ \Omega$ cm) Si were cut to provide Au–n-Si Schottky barrier structures. $C(U)$ profiling revealed uniform donor concentrations in the range of (6 to 9) $\times 10^{13}$ cm^{-3}. The specimens were irradiated with 1.5 MeV electrons at doses around 10^{15} e$^-$/cm^2 near room temperature. DLTS measurements were carried out with a standard lock-in spectrometer as that described by Ferenczi et al. [1]. The depth profiles of the levels and the electric field dependence of their emission rate were obtained by using the differential DLTS approach [1].

---

[1] 104, Solonos Str., 10680 Athens, Greece.

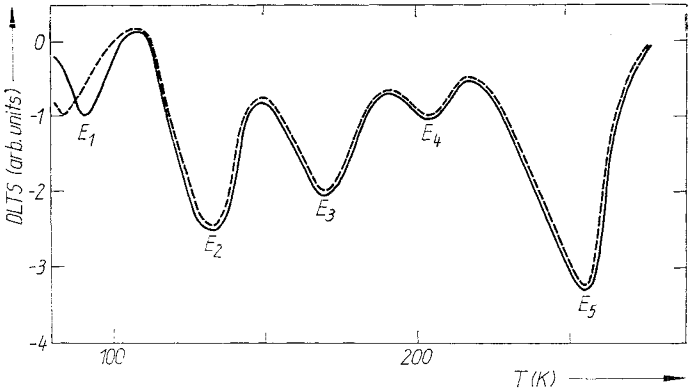

Fig. 1. Two temperature scans of phosphorous-doped, electron-irradiated Si, arising from two different positions in the space charge region specified by the reverse bias U_R and the two filling pulses U_1 and U_2. (a) solid line $U_R = -20$ V, $U_1 = 0$ V, $U_2 = -5$ V; (b) dashed line $U_R = -20$ V, $U_1 = -15$ V, $U_2 = -20$ V

3. Results and Discussion

Fig. 1 presents the typical DLTS spectrum obtained after electron irradiation of n-Si. Five majority traps were observed. Cumulative Arrhenius plots for the thermal emission rates corrected with the inverse square of the temperature versus the inverse temperature are shown in Fig. 2. The activation energies derived from the plots E_1 (E_c – 0.15 eV), E_2 (E_c – 0.21 eV), E_3 (E_c – 0.28 eV), E_4 (E_c – 0.33 eV), E_5 (E_c – 0.45 eV) represent energy positions in the gap relative to the conduction band edge providing that the capture cross-sections are temperature independent. Capture cross-sections were found by measuring the peak amplitudes for different pulse widths in the frequency scan mode [2]. Fig. 3a shows some representative frequency scans for E_3 and E_4 for different pulse durations, while in Fig. 3b the corresponding capture cross-section analysis is depicted. In the latter figure S denotes the DLTS output for a pulse width t_p and S_0 the saturated DLTS output for very long pulse widths.

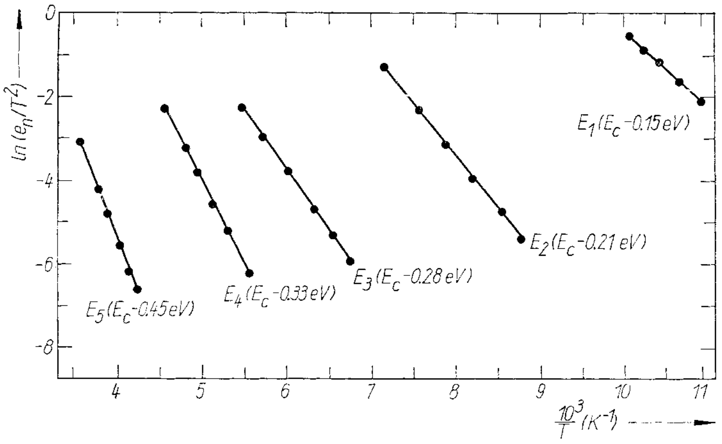

Fig. 2. Arrhenius plots of the observed levels in n-Si

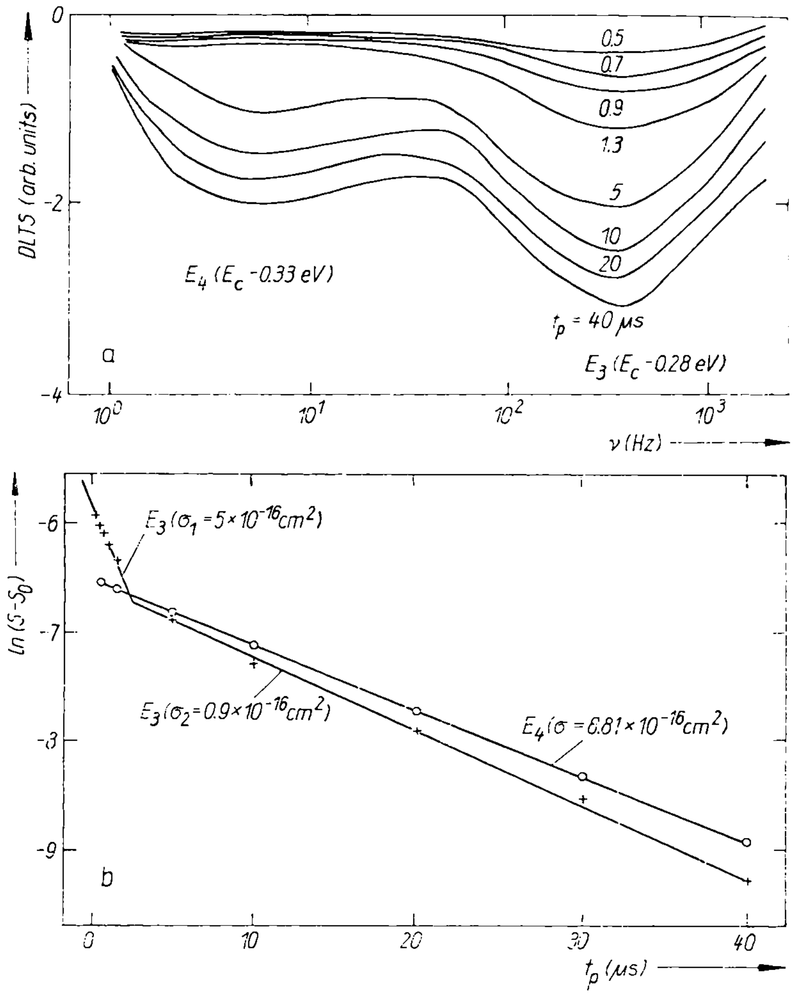

Fig. 3. a) Representative frequency scans of the peaks E_3 and E_4 for different pulse durations at $T = 120$ K. b) Capture cross-section analysis for the peaks E_3 and E_4

A search for metastable properties of the levels with respect to electrical excitation gave negative results. No changes were observed in the spectra when cooling the samples from a certain T either with or without the application of a reverse bias prior to beginning the DLTS pulsing.

The depth distribution of the defect states was also investigated. Concentration profiling of the E_1, E_2, E_3, E_4 levels revealed uniform distributions throughout the depletion region as expected for electron irradiations. The depth profile of the E_5 level, however, exhibited an unexpected inhomogeneity at around 2.3 μm. Such a profile is usual for ion implantation and we cannot say if a non-flat quasi-Fermi level or some other mechanism is responsible for its appearance. Fig. 4 presents the concentration profile of E_3 (the profiles of E_1, E_2, and E_4 are similar to E_3) and E_5.

Activation energies and capture cross-sections of the levels resulting from these studies are summarized in Table 1. In the following we shall discuss each level separately.

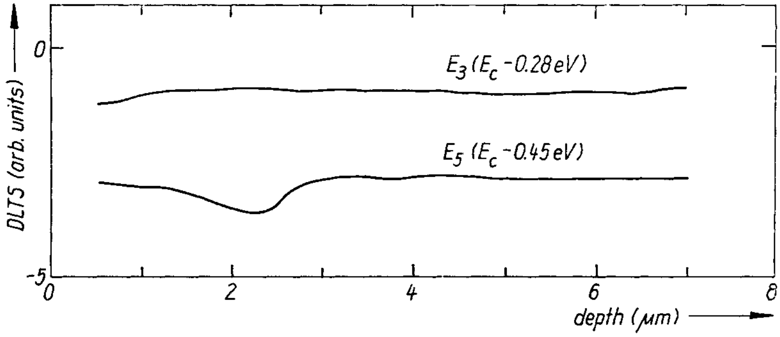

Fig. 4. Depth profiles of the E_3 and E_5 peaks

3.1 E_c —0.15 eV

The centre E_1 at $E_c - 0.15$ eV is first worth considering. In the same energy region of the gap produce levels the V + O pair [3 to 5], usually called the A-centre and the $C_i - C_s$ pair [6, 7]. Defects of undetermined nature have also been reported in electron- and neutron-irradiated silicon [8, 9]. Due to its weak DLTS signal and the fact that only at very short pulse durations ($t < 2$ μs) we were able to observe changes in the peak amplitude of E_1 the capture cross-section analysis gave a rather poor linearity with an estimated cross-section around 10^{-15} cm^2. Although the thermal parameters only are not adequate to provide the indentity of a trap we believe that the above values of activation energy and capture cross-section point to the A-centre. The small concentration of the peak E_1 is probably due to the small oxygen content of our samples.

The A-centre is considered as acceptor-like (—1/0) because no field-assisted electron emission process (the well-known Poole-Frenkel effect) was detected for it [10]. This behaviour is expected for a centre which becomes neutral after emission. Although a donor-like centre as the EL_2 in GaAs may exhibit similar behaviour [11] if its capture cross-section is thermally activated, this is not the case for the A-centre [12]. The

Table 1

Electrical parameters of radiation-induced deep levels in P-doped Si

defect state	activation energy	capture cross-section (cm^2)	T[a]) (K)	identification	ref.
E_1	$E_c - 0.15$ eV	$\approx 10^{-15}$	90	V + O (A-centre)	[3 to 5, 10, 12 to 14, 18, 19]
E_2	$E_c - 0.21$ eV	3.53×10^{-17}	115	$V_2^=$	[3 to 5, 19, 20, 22]
E_3	$E_c - 0.28$ eV	0.91×10^{-16} 5.03×10^{-16}	120	V-related centre (V_2O, V + C) (?)	[3, 20, 30, 31]
E_4	$E_c - 0.33$ eV	8.81×10^{-17}	120	V_2-related centre (V_2O_2) (?)	[4, 5, 32, 33, 34]
E_5	$E_c - 0.45$ eV	1.1×10^{-16} 3.17×10^{-16}	272	V + P (E-centre) V_2^-	[3 to 5, 9, 18, 20, 22 to 27]

[a]) Temperature where the capture cross-section analysis was made.

acceptor character of the A-centre has also been inferred [13] by monitoring, during irradiation, the resonance of the trap and that of phosphorus in phosphorus-doped Si. We should notice, however, that a careful study of the A-centre signal presented in [10] reveals small shifts of the peak position towards lower temperatures with increasing reverse bias. In our measurements a small enhancement of the electron emission rate by the junction electric field was also observed. Fig. 1 shows two temperature scans for different regions of the depletion charge layer specified by different amplitudes of the two applied filling pulses. The position of the E_1 peak shifts to lower temperatures for higher electric fields. These observations are not consistent with a Poole-Frenkel model employing a Coulomb potential since such a potential between a defect state which becomes neutral after emission and a charged carrier simply does not exist. Irmscher et al. [14] have also observed an influence of the electric field on the emission rate of the A-centre and they explained their results with the phonon-assisted tunneling model [15] However, the agreement between their experimental data and the theory was implying the use of values for the fitting parameters, the physical meaning of which needs further investigation. In their model they have used a pure Dirac potential well. It is known that various potentials exhibit quite different field dependences [16]. Deep centres are expected in general to be non-Coulombic. Lax [17] in order to account for the capture of carriers by neutral impurities used a polarization potential of the form $U(r) = -A/r^4$. Neglecting the Jahn-Teller distortion the V + O pair is virtually an oxygen substitutional and a polarization potential could be assigned to it [18]. Certainly, in reality more general barrier shapes should be considered. We believe that the polarization potential deserves considerable attention as a physically plausible idea when trying to explain the electric field dependence of the A-centre.

3.2 E_c —0.45 eV

Secondly we shall comment on the E_5 level at $E_c - 0.45$ eV. From the plot of $\ln(S - S_0)$ versus t_p, which gave two straight branches, it is inferred that two centres with close energy positions in the gap but different capture cross-sections contribute to the formation of the corresponding DLTS peak. These centres according to previous reports [5, 19] should be the P + V pair usually called E-centre and the single negative charge state of the divacancy V_2^-. It is worth noticing that these two centres have also been identified as producing separate neighbouring peaks in the DLTS spectrum [20]. The energies assigned to both centres range in the literature from $E_c - 0.38$ eV to $E_c - 0.48$ eV. Reported capture cross-section generally give [5] a larger value for the P + V pair than for the V_2^-. Therefore, we may tentatively correlate the measured value 1.1×10^{-16} cm^2 of the capture cross-section with the E-centre and that of 3.17×10^{-17} cm^2 with V_2^-.

It is worth noticing that recent DLTS measurements combined with minority current injection have revealed [21] the presence of a third trap, tentatively attributed to a phosphorus–carbon (P + C) pair, which also contributes to the same DLTS peak as the P + V pair and V_2^-. This defect, however, appears as a major radiation-induced defect in heavily-doped silicon material ($n \geqq 10^{16}$ cm^{-3}) which is not our case here.

3.3 E_c —0.21 eV

The defect state E_2 ($E_c - 0.21$ eV) is not well understood so far. There is a general tendency in the literature to correlate it with the doubly negative charge state of the divacancy on the basis of introduction and annealing rate data [22]. The proportionality of the strengths of the DLTS signal of the $E_c - 0.23$ eV and $E_c - 0.41$ eV levels at different depths is a strong indication that they originate from different charge states of the same defect centre [20]. However, there are some controversies and points of confusion as regards these assignments. From photoconductivity studies [23], for example, it has been found that the divacancy-associated states in n-type Si are at $E_c - 0.39$ eV and $E_c - 0.54$ eV whereas the level at $E_c - 0.22$ eV has shown a behaviour not associated with the same divacancy transition exhibiting by the other two levels. The infrared optical absorption peak at 0.34 eV in Si is usually associated with V_2^-. Recent optical studies [24] have shown that when this charge state is populated by electrons a defect level at $E_c - 0.54$ eV is one of the levels from which these photoexcited electrons originate. It is worth noticing at this point that a recent theoretical analysis of experimental data [25] has concluded that assignments to the divacancy of levels different than those at $E_c - 0.23$ eV and $E_c - 0.39$ eV in the upper half of the band gap should be considered as incorrect. On the other hand, the observation that capacitance measurements gave different introduction rates for the levels at $E_c - 0.23$ eV and $E_c - 0.39$ eV has been used [9] as an indication that these levels belong to different defects. A possible solution of this contradiction could be the fact that two defects are the source of the peak at $E_c - 0.39$ eV although only one capture cross-section is reported there.

Uniaxial stress-DLTS experiments for a level at $E_c - 0.23$ eV observed in neutron-irradiated n-type Si have also shown results [26] which could hardly be reconciled with the divacancy. Defect profiling measurements [27] have also cast strong doubts on the assignment of the $E_c - 0.25$ eV level with V_2^-. Measurements of the temperature dependence of the Hall coefficient [28, 29] have shown that a defect state at $E_c - 0.22$ eV might be correlated with the V_2O complex in γ-ray- and electron-irradiated n-Si.

The exceptionally large capture cross-section ($\sigma = 2 \times 10^{-16}$ cm^2) for electron trapping on level $E_c - 0.23$ eV has led Kimerling [3] to consider its attribution to $V_2^=$ as somewhat dubious. Moreover if E_2 is related to $V_2^=$, it should have a much smaller capture cross-section than that of V_2^-. These facts point against a Coulomb potential for the divacancy. Indeed, the divacancy is considered as highly distorted and the Coulomb force may not be the important factor in the process of electron capturing [22]. In addition to the repulsive Coulomb-like potential the electron may also experience a contribution of an attractive potential of unknown nature. It has also been proposed [18] that the divacancy may have a dipole or even a quadrupole potential. This suggestion seems quite reasonable since this defect is formed when two neighbouring Si atoms are knocked out and the lattice is reconstructed such that there is a clear charge separation. We should also note that a weak electron field dependence of the emission rate reported [18] for the two V_2 levels at $E_c - 0.23$ eV and $E_c - 0.41$ eV has not been observed in our studies. It is obvious that a complete understanding of the electrical activity of V_2 needs further investigations.

3.4 E_c —0.28 eV and E_c —0.33 eV

These two distinct defect states will be discussed together since only speculative assignments exist in the literature for levels in this energy region. A defect state at $E_c - 0.30$ eV has been tentatively correlated previously with the V_2O centre [3, 30]. A broad peak possibly originating from the contribution of two overlapping centres has been detected at $E_c - 0.31$ eV [20, 31]. The first centre has been correlated with gold complexes on the basis that gold is the material of the Schottky contact. The second level has been tentatively attributed to a vacancy and carbon-related complex.

In connection with the E_4 level at $E_c - 0.33$ eV we should notice that an unidentified level has been reported in this position previously [4, 32, 33]. A centre at $E_c - 0.34$ eV was considered as V_2-related [5]. A level with activation energy $E_c - 0.36$ eV has been tentatively assumed to be the V_2O_2 complex [34]. The present data do not allow a certain identification of the emitting centre. It might be a complex comprising a primary defect in association with other lattice imperfections. This assumption is reasonable since secondary processes are of primary importance in the formation of stable defects in room-temperature irradiated silicon.

In conclusion, we have investigated the electrical properties of the levels appearing in irradiated Si. Although a large amount of information has been gathered during the last twenty years and substantial progress has been achieved the complete picture is still lacking. The large capture cross-section of $V_2^{=}$ is not yet fully understood. The exact chemical identity and microscopic structure of other defect states usually appearing in the spectra is not known. Further investigations based on a combination of experimental techniques is needed to resolve the remaining problems.

Acknowledgements

The author wishes to thank Dr. G. Ferenczi of the Technical Institute of the Hungarian Academy of Sciences for providing the research facilities to carry out this experiment in the framework of the bilateral agreement between Greece and Hungary.

References

[1] G. Ferenczi, P. Krispin, and M. Somogyi, J. appl. Phys. **54**, 3902 (1983).
[2] G. Ferenczi, J. Boda, and T. Pavelka, phys. stat. sol. (a) **94**, K119 (1986).
[3] L. C. Kimerling, Radiation Effects in Semiconductors, Ed. N. B. Urli and J. W. Corbett, IOP Conf. Ser. No. 31, Bristol/London 1977 (p. 221).
[4] L. C. Kimerling, P. Blood, and W. M. Gibson, Defects and Radiation Effects in Semiconductors, Ed. J. H. Albany, IOP Conf. Ser. No. 46, Bristol/London 1979 (p. 273).
[5] S. D. Brotherton and P. Bradley, J. appl. Phys. **53**, 5720 (1982).
[6] L. I. Murin, phys. stat. sol. (a) **93**, K147 (1986).
[7] L. W. Song, B. W. Brower, and G. D. Watkins, Appl. Phys. Letters **51**, 1155 (1987).
[8] P. M. Mooney, J. Appl. Phys. **54**, 208 (1983).
[9] Y. Tokuda, N. Shimirn, and A. Usani, Japan. J. appl. Phys. **18**, 309 (1978).
[10] J. L. Benton, L. C. Kimerling, and M. Stovala, Physica **B116**, 271 (1983).
[11] W. R. Buchward and N. M. Johnson, J. appl. Phys. **64**, 958 (1988).
[12] G. A. Samara, Phys. Rev. B **35**, 4841 (1987).
[13] G. D. Watkins, J. W. Corbett, and R. M. Walker, J. appl. Phys. **30**, 1198 (1959).
[14] K. Irmscher, H. Klose, and K. Maass, phys. stat. sol. (a) **75**, K25 (1983).
[15] S. Makram-Ebeid and M. Lannoo, Phys. Rev. B **25**, 6406 (1982).
[16] P. A. Martin, B. G. Streetman, and K. Hess, J. appl. Phys. **52**, 7609 (1981).
[17] M. Lax, Phys. Rev. **119**, 1502 (1960).
[18] Z. F. Guan, G. P. Li, K. L. Wang, and F. Chang, Proc. Symp. Defects in Silicon, Ed. W. M. Bullis and L. C. Kimerling, The Electrochem. Soc., Vol. 83, Pennington (N.J.) 1983 (p. 491).
[19] J. R. Troxell, Solid State Electronics **26**, 539 (1983).
[20] B. G. Svensson and M. Willander, J. appl. Phys. **62**, 2758 (1987).
[21] A. Chantre, J. L. Benton, M. T. Assom, and L. C. Kimerling, Mater. Sci. Forum **10/12**, 1111 (1986).
[22] A. O. Evwaraye and E. Sun, J. appl. Phys. **47**, 3776 (1976).
[23] A. H. Calma and J. C. Corelli, Phys. Rev. **173**, 734 (1968).
[24] J. Svensson, B. G. Svensson, and B. Monemar, Phys. Rev. B **38**, 4192 (1988).
[25] A. V. Vasilev, L. S. Smirnov, and S. S. Shalmeev, Soviet Phys. — Semicond. **20**, 465 (1986).

[26] J. W. FARMER, J. M. MEESE, P. M. HENRY, and C. D. LAMP, Proc. 13th Int. Conf. Defects in Semiconductors, Ed. L. C. KIMERLING and J. M. PALLEY, AIME, New York 1985 (p. 639).
[27] K. L. WANG, H. H. LEE, and J. W. CORBETT, Appl. Phys. Letters **33**, 547 (1978).
[28] L. A. KARAKEVICH, V. I. KUZNETSOV, and P. E. LUGAKOV, Radiat. Eff. Letters **87**, 147 (1986).
[29] I. P. KOZLOV, A. G. LITVINKO, P. E. LUGAKOV, S. V. MISHUK, and V. D. TKACHEV, Soviet Phys. – Semicond. **6**, 1743 (1973).
[30] A. O. AWADELKARIM, H. WEMAN, B. G. SVENSSON, and J. L. LINDSTRÖM, J. appl. Phys. **60**, 1974 (1986).
[31] B. G. SVENSSON, B. M. S. LARSSON, and K. H. RUDEN, Proc. 15th Internat. Conf. Defects in Semiconductors 1988, to be published in Mater. Sci. Forum.
[32] J. W. WALKER and C. T. SAH, Phys. Rev. B **10**, 4587 (1973).
[33] L. C. KIMERLING, IEEE Trans. Nuclear Sci. **23**, 1497 (1976).
[34] J.-G. XU, F. LU, and H.-H. SUN, Phys. Rev. B **38**, 3395 (1988).

(Received January 30, 1989)