Electron capture at the two acceptor levels of a zinc center in silicon

Alex C. Wang, Luke Su Lu, and C. T. Sah
Department of Electrical Engineering and Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
(Received 8 May 1984)

Electron-capture rates in zero electric field at both zinc acceptor levels have been directly and accurately measured by the transient-capacitance techniques for the first time. The data elucidate two major outstanding questions in recombination physics: (1) It has been suspected for two decades that the carrier capture rates associated with many centers with multiple charge states were due to a local Auger mechanism. We show that this postulate can be experimentally tested by the double-pulse method, and in the case of Zn in Si the Auger effect plays a negligible role. (2) While several workers have stressed that the electronic barrier may be more important than the vibronic barrier in determining the temperature dependence of carrier-capture rates at repulsive centers below room temperature, the charge effect was usually ignored in the literature. We show that in the case of Zn in Si, tunneling through the screened Coulomb barrier controls the temperature dependence below 200 K and above which tunneling through the vibronic barrier becomes important. Overall, the effect of the electronic barrier below room temperature is predominant and it gives a temperature-dependent capture rate that can be easily mistaken as the occurrence of a multiphonon-emission mechanism. Failure to recognize the charge effect may result in fitting of trap parameters inconsistent with physical reality.

I. INTRODUCTION

Carrier capture at deep-level trapping centers in semiconductors has been under active investigation for over three decades.[1-3] The study of the capture phenomenon is of fundamental importance since it explores the energy-exchange mechanisms involved in the band-to-bound transitions, one of the principal problems in solid-state physics. Its understanding is also of great practical interest since the carrier-capture rates control the recombination-trapping kinetics,[4-6] which has profound effects on device operation.[1]

As recently reviewed by Stoneham,[7] the state of knowledge in this area is far from adequate. The lack of good understanding was partly due to the absence of reliable and accurate experimental methods before the development of the capacitance and current transient techniques.[8,9] On the other hand, it should be mentioned that a better understanding has also been hampered because most research efforts have concentrated on deep centers of unknown atomic origin, e.g., the A, B, and EL2 centers in GaAs.

In this work we wish to elucidate two major outstanding questions: (1) Is a local Auger mechanism[3,10,11] responsible for carrier capture at many centers with multiple charge states? (2) How important is the electronic barrier on the temperature dependence of capture rates at repulsive centers?[2,7,12-15] Electron-capture processes at the zinc double-acceptor center in silicon are ideally suited to answer these questions and were therefore chosen for this study. We have measured these capture rates in zero electric field at both zinc levels directly and accurately by the capacitance transient technique[8,9] for the first time.

Our results clearly show that, in the case of Zn in Si, the Auger mechanism makes a negligible contribution to the capture rate, but also that the repulsive potential is the dominant factor below room temperature. The latter has serious implications in the interpretation of the capture rates in the nonradiative-multiphoton-emission (NMP) mechanism.[7,13-15]

The choice of Zn in Si was made from following the philosophy of "try the simplest case"[16] to clarify a controversial issue. Si is chosen since its properties are best characterized to date, and as an elemental semiconductor it is free of unavoidable native defects in compound semiconductors. To probe the effect of the long-range repulsive barrier, simple free-carrier states are preferred. Thus, electron-capture processes are studied, since in Si, hole states are considerably more complex than electron states.[17-20] A double acceptor is required in order to give the negatively charged repulsive level and local Auger effect. Zn is the obvious choice because it has been established as a well-behaved simple substitutional impurity which gives the double-acceptor levels according to the valence-bond model.[21-27] This choice is further supported by the similar double-acceptor nature of Zn in Ge.[28,29] Being heavier than Si, Zn cannot produce local-phonon modes, and so comparison of experiments with the NMP mechanism of the current theory is simplified.[30]

Knowledge of Zn in Si is also of technological importance. One commercial process for the production of semiconductor-grade Si used Zn to reduce silicon tetrachloride.[31] Although this process has apparently been completely supplanted in the United States by various hydrogen-reduction methods, there has recently been a revived interest in producing low-cost silicon stock by zinc-vapor reduction of silicon tetrachloride in a fluidized bed for solar photovoltaic application. Large amounts of zinc

impurity remain in the granular silicon. The zinc residue acts as recombination centers and reduces the efficiency of solar cells fabricated on such silicon materials.[25] On the other hand, Zn-doped Si is a promising high-performance infrared detector capable of monolithic integration with digital and analog circuits on a silicon chip.[32] Our finding that a local Auger effect is unimportant is particularly essential to a successful modeling of recombination. This is because such electron Auger capture removes two bound holes in a single transition,[10] and therefore is a process not described by classic Sah-Shockley multilevel kinetics.[6]

II. EXPERIMENTAL DETAILS

The new capture-rate data in this work were measured on the zinc-diffused p^+/n diode P24-Z8-7 fabricated by Herman.[21] Its processing procedures were described in detail in Ref. 21. The diode has a metal-oxide-semiconductor (MOS) guard ring to ensure that the signals measured come only from the diode and not from any surface channel. In the n-base region used in capture-rate determination, the phosphorus doping was 1.14×10^{16} cm^{-3} and the zinc concentration was 8.0×10^{14} cm^{-3} as determined by depletion C-V and transient-capacitance analysis.[33]

The capture rates were measured by the double-pulse method.[9] In these measurements a high-injection forward-bias pulse was first applied to the reverse-biased diode to fill both zinc levels with holes. A filling pulse that did not forward-bias the diode followed to allow the majority carriers (electrons) to fill the levels we are concerned with. The capture rates were determined from the dependence of the size of capacitance transients on the pulse width of the second pulse. The reverse dc bias used was 8 V, and the filling pulse reduced the reverse bias to 1.5 V during the pulse. We used a Hewlett-Packard HP-8165A Programmable Pulse Generator terminated in a 50-Ω load to deliver the voltage pulses. The pulse generator has a minimum pulse width of 10 ns with rise and fall times shorter than 5 nsec and pulse overshoot of less than 5% of the amplitude, which were quite adequate for this measurement. Its pulse width was found to deviate by less than 1% from the programmed value.

The capacitance transient technique, unlike other methods such as photoconductivity decay,[1] is uniquely unambiguous. At higher temperatures, when the hole-emission transients were recorded, the emission rates were obtained at the same time as the capture rates. The capture rates were definitely due to zinc since the emission rates were identical to the data of Herman and Sah.[21] The capture rates at lower temperatures, when trapped holes were frozen, were measured by the multiple-pulse method, i.e., by monitoring the static capacitance change after each of the many filling pulses applied in succession. They can still be assigned to zinc unambiguously by continuity in temperature dependence to the higher-temperature data.

The carrier freeze-out, or impurity-deionization effect,[34] was taken into account. The electron density-of-states effective mass m_N was computed from the empirical formula[25]

TABLE I. Si:Zn recombination parameters at room temperature (24.0 °C=297.15 K).

Parameter (unit)	Values
Energy level E_V+664 meV	
c_{n1} (cm^{3}s^{-1})	$(2.4\pm0.5)\times10^{-12}$
e_{n2} (s^{-1})	0.49 ± 0.19
c_{p2} (cm^{3}s^{-1})	$(5.9\pm0.6)\times10^{-8}$
e_{p1} (s^{-1})	29 ± 2
Energy level E_V+326 meV	
c_{n0} (cm^{3}s^{-1})	$(2.3\pm0.3)\times10^{-8}$
e_{n1} (s^{-1})	$(5.1\pm2.1)\times10^{-3}$
c_{p1} (cm^{3}s^{-1})	$(4.9\pm0.7)\times10^{-8}$
e_{p0} (s^{-1})	$(2.2\pm0.3)\times10^{7}$

$$m_N/m=1.0617[1+(T/142.7)^3][1+(T/202.1)^3]\times\{[1+(T/166.8)^3][1+(T/193.5)^3]\}^{-1},$$

where m is the free-electron mass and T is the absolute temperature in degrees Kelvin. Values from this formula have substantial experimental support.[25] More accurate future effective-mass data are not expected to be very different from this fit of older data, and will not alter the results deduced from our considerations to be given.

Table I is a summary of recombination parameters of Zn in Si at room temperature (24.0 °C). The table is identical to that of Sah *et al.*,[25] except that the more accurate c_{n1} value from this work is listed and e_{n2} is changed accordingly. The least-squares-fit equations of the eight capture and emission rates are given in the Appendix for ease in future device application.

III. RESULTS AND DISCUSSION

We will first discuss electron capture at the second acceptor level, as its measurement lends to the argument concerning the mechanism for electron capture at the first acceptor level.

A. Electron-capture rate c_{n1} at second acceptor level (E_V+664 meV)

The c_{n1} data obtained in this work are shown in Fig. 1. Also shown for comparison are data of Sklenski and Bube[22] from optical quenching of photoconductivity at an electron density of 3×10^{14} cm^{-3}. Their method was indirect and subject to larger error, as is evident from Fig. 1. The general trends agreed, however, in that the rate was more or less thermally activated above 100 K but appeared to have leveled off at lower temperatures.

Sklenski and Bube did not attempt detailed quantitative interpretation due to the rather large experimental uncertainties in their data. They did speculate that the c_{n1} behavior might be due to the repulsion of the electrons by the negatively charged zinc center.

This speculation is well grounded. The repulsive Coulomb potential should be an effective barrier for electrons because of its long-range character. In fact, the unscreened Coulomb field has an infinite scattering cross

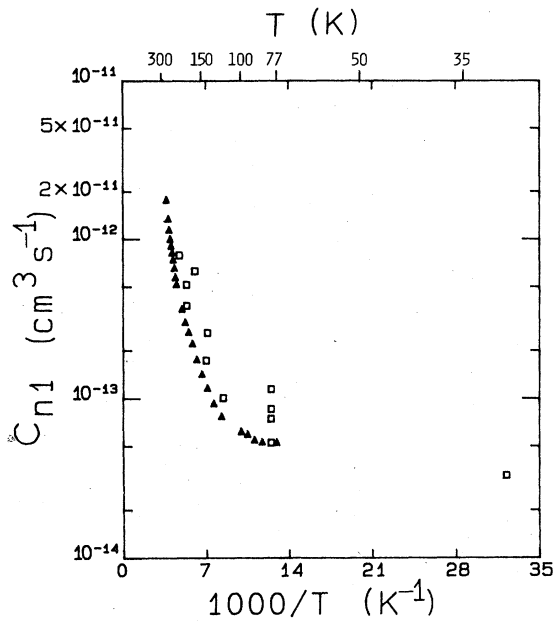

FIG. 1. Temperature dependence of c_{n1}. Triangles, this work; squares, from Sklenski and Bube (Ref. 22).

section.[36] It seems only natural that this force has been invoked to explain the photoconductive response of sensitizing centers,[37] delay of stimulated emission in laser diodes,[38] charge transport in polysilicon,[39] and persistent photoconductivity,[7] among other phenomena. Despite the obvious physics, this charge effect is often ignored in the recent literature concerning carrier-capture rates.

The problem of electron tunneling through the Coulomb barrier was solved in 1931 by Sommerfeld.[36] The thermal averaging in Boltzmann statistics was treated by Bonch-Bruevich and Landsberg,[12] and Paessler.[13,40] The probability, or thermally averaged Sommerfeld factor, that an electron approaches the immediate vicinity of a singly negatively charged deep center is[40]

$$F=(8/9\sqrt{3})(T_0/T)^{2/3}\exp[-(T_0/T)^{1/3}]\,, \qquad (1)$$

where $T_0=56\pi^4 m_N e^4/\epsilon^2 h^2 k$, e is the electron charge, ϵ is the permittivity of the semiconductor, h is Planck's constant, and k is Boltzmann's constant.

Since the bound-state wave function is quite localized for a deep level, the conduction-electron wave functions determine the capture rate predominantly by their amplitudes near the center. The effect of the Sommerfeld factor given by Eq. (1) is therefore simply to reduce the capture rate by F, below that when there is no repulsive barrier, i.e., when the center is neutral. Note that the above argument did not specify the mechanisms (multiphonon emission, radiative, etc.) for the "neutral part" of the capture process, nor did it refer to any details of a particular deep center. This separation of charge effect into a mechanism- and trap-independent factor is clearly very desirable.

Despite the simplicity of Eq. (1), it has long been noted only by experimentalists.[12,37] In Ge, electron capture at Be^- simply followed the temperature dependence governed by Eq. (1). We will show that the Sommerfeld factor is also dominant in our present case.

We first evaluate F given by Eq. (1) using $\epsilon=11.8$ for Si. This is plotted in Fig. 2. Two points are to be noted. First, the size of F—it means that the capture rates at repulsive centers should be a few orders of magnitude smaller than those at neutral centers. Second, F appears to be thermally activated if a small range of temperature is considered. This is particularly so at low temperatures. Both of these points are long-standing experimental facts.[2,12,41] They have important consequences in interpreting capture rates, as will be discussed later.

To find out if the Sommerfeld factor controls the dependence of c_{n1} in a certain temperature range, we see from Eq. (1) that a semilogarithmic plot of $c_{n1}T^{2/3}$ versus $T^{-1/3}$ is a convenient indicator. This is shown in Fig. 3. It becomes clear that between 100 and 200 K a straight line is a good approximation, but c_{n1} leveled off below 100 K and had additional activation above 200 K. To confirm that the T_0 is simply a combination of fundamental or first-principles parameters of silicon, we compute the "neutral part" of the capture rate, i.e., c_{n1}/F, where F was that plotted in Fig. 2. The neutral c_{n1}^0 is shown in Fig. 4, in which data at $T<100$ K were not included to avoid confusion since another mechanism to be discussed later is important. The plateau $200>T>100$ K is a good verification that the Sommerfeld factor essentially controls the temperature dependence of c_{n1} in this range.

Figure 4 is instructive. The size of c_{n1}^0 at the plateau is several orders of magnitude greater than what would be expected for radiative capture.[2] As an example, the radiative electron-capture rate of the neutral indium in Si is only 5×10^{-15} $cm^3 s^{-1}$.[42] This means that the capture must be nonradiative. The temperature dependence of c_{n1}^0 has the general shape as in the NMP mechanism,[14] which we pursue later.

We turn to the behavior of c_{n1} at $T<100$ K. It first

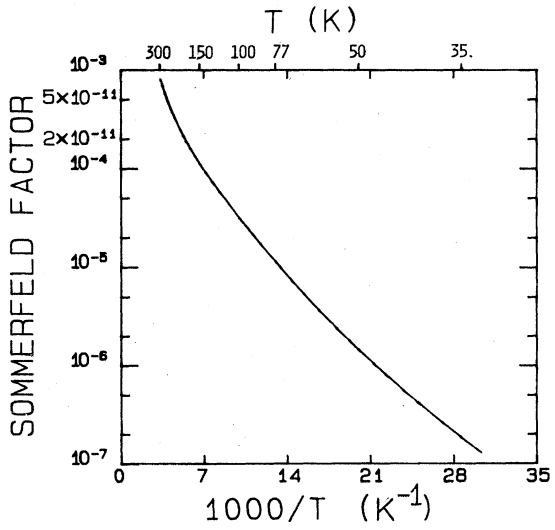

FIG. 2. Temperature dependence of Sommerfeld factor for electron capture at a singly negatively charged deep center in silicon.

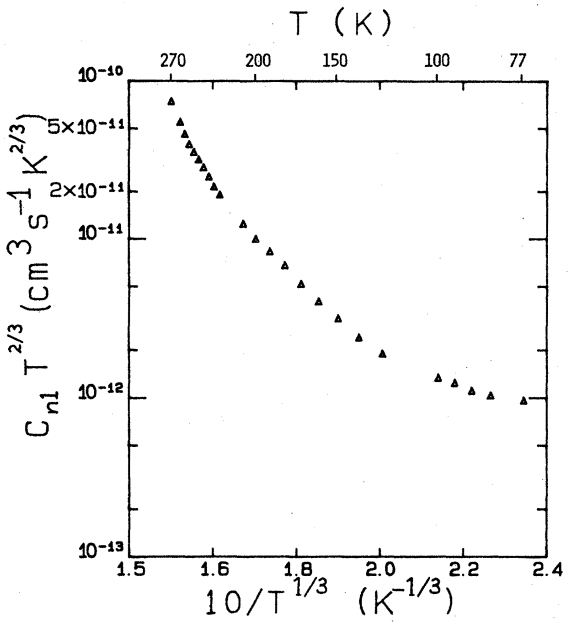

FIG. 3. Temperature dependence of $c_{n1}T^{2/3}$.

appeared puzzling. The leveling-off at low temperature is reminiscent of the debate on electron capture at the B center in GaAs.[7,43,44] There, by arbitrarily assuming that the center was neutral, radiative[43] and free-carrier Auger[44] mechanisms were invoked. Now that we know that the zinc center is definitely negatively charged, neither of their hypotheses is applicable. The contribution of radiative capture was already ruled out by its magnitude. Furthermore, the Sommerfeld factor should control radiative capture[12,15,45] just like nonradiative processes. In fact, the electron capture at Be^- in Ge, which simply followed the Sommerfeld factor, was purely radiative.[40] The overlap of the wave functions of the bound state and conduction-electron states appears in both the Coulomb integral and the exchange integral,[2] so the charge effect

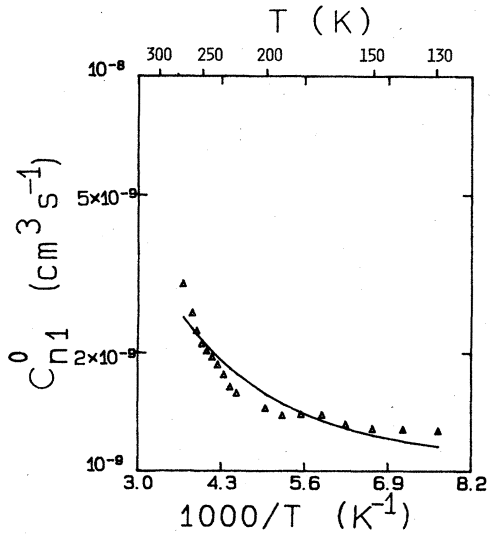

FIG. 4. Temperature dependence of c^0_{n1}.

must also be present in free-carrier Auger capture. Moreover, at $T < 100$ K significant deionization occurred. At 77 K the electron concentration dropped to about one-third of the phosphorus doping. Owing to the characteristic concentration dependence, the free-carrier Auger capture rate could only further reduce the capture rate.

In principle, phosphorus-zinc pair recombination could occur in the deionization temperature range and make the apparent electron-capture rate large.[46] The antimorph of recombination at the shallow-acceptor—deep-double-donor-pair complex has been discussed by Dean.[47] In our case the rate is probably many orders of magnitude too small since the pair separation is very large.[48]

The puzzling behavior just described can be explained by the long-ignored work of Rogachev and Ryvkin.[49] They clearly showed that, at common doping levels, the capture rate at a repulsive center must level off at low temperatures due to screening of the Coulomb barrier by free carriers and ionized dopant impurities. We note that the Debye length[50] in our diode is about 200 Å at 100 K, which is of the same order as the distance where the average kinetic energy of an electron (kT) equals the Coulomb potential energy. Quantitative derivation of the temperature dependence in this range will not be attempted since the Boltzmann averaging of tunneling rate through a three-dimensional Yukawa potential mediated by random ionized impurities is analytically untractable.[49,51] Our recognition of the screening effect has the following important bearings.

(i) The very fact that screening is at work for repulsive centers is proof that the capture is carried out by quantum-mechanical tunneling, not classical barrier surmounting,[22,37] since screening has a negligible effect on the barrier height.[49]

(ii) Recent work on carrier capture[13,15,30] neglected screening. This is not justified for most experimental samples at low temperature, except perhaps for semi-insulators.[49] For repulsive centers the activation of capture rate due to thermal averaging of Coulomb tunneling, and its low-temperature plateau due to screening, give a feature which could be expected if the temperature dependence is due to tunneling through the vibronic barrier in the NMP mechanism.[14] This is very misleading since fitting to the NMP theory would result in trap parameters completely inconsistent with physical reality. Since the electron-capture rate at the B center in GaAs (Refs. 7, 43, and 44) has a magnitude and temperature dependence similar to our c_{n1} data in Fig. 1, the interpretation in terms of only NMP, given in the literature, may deserve reinvestigation. For attractive centers, screening can destroy the high Rydberg series of the excited states, so modification of the recent phonon-cascade theory[2,7] is necessary.

(iii) In the literature the common interpretation of a small temperature-independent capture rate is that the center is neutral and the capture is radiative.[1,37] This is misleading since a repulsive center also has a small capture rate due to the Sommerfeld factor and it is temperature independent at low temperatures due to screening.

(iv) The electron-capture rate at Zn^- in Ge obtained by Pokrovky[46] between 20 and 45 K is now easy to under-

stand. It was measured on n-type Ge samples doped with about 5×10^{16} Sb atoms/cm^3 and 10^{15}–10^{16} Zn atoms/cm^3. The rate was 3×10^{-14} cm^{3}s^{-1} and was independent of temperature. Its magnitude was close to our c_{n1} data shown in Fig. 1 at 77 K and indicated the similarity between the two double-acceptor systems. The temperature independence was simply due to screening. Although Pokrovsky[46] could detect extrinsic radiation from his Zn-doped n-type Ge samples, it was not a quantum efficiency measurement and his suggestion that the rate was radiative is in doubt.

(v) The photocapacitance measurement[8] has become a powerful technique capable of revealing trap properties not obvious from purely electrical measurements.[52] The interpretation of photoionization cross-section data is, however, often strongly dependent on the theory.[15,20,21,45,53–56] It was not until the work of Ridley and Amato[15,45] that the charge effect received attention. They ignored the screening, but since photocapacitance must be measured at low temperature when trapped charges are frozen,[8] screening must be considered. This may partly account for Ledebo's observation[20] that the experimental photoionization spectra did not seem to depend as strongly on the charge as one would expect. In the context of carrier capture, the proper interpretation of the spectra is essential, since, in principle, the spectra contain information pertaining to configuration-coordinate (CC) diagrams which are extensively used to invoke the NMP mechanism.[7,15,53,54]

Now we return to the "neutral" capture rate shown in Fig. 4. Having ruled out any significant radiative and free-capture Auger contributions, we must attribute this to NMP.[54] Henry and Lang[54] used a semiclassical approach and obtained a major result, namely that capture rates due to NMP should be simply thermally activated at high temperature, which was invoked to explain a large amount of data on traps in GaAs and GaP. A consensus has been reached,[14,30,40,57] however, that the usual experimental temperature is too low for the Henry-Lang semiclassical result[54] to be applicable. As shown in Fig. 2, the electronic barrier alone can cause substantial thermal activation. Additional activation is available from the low- or medium-temperature NMP mechanism.

As will be justified later, the proper current theoretical formula that describes our case is the low-temperature formula[14,30]

$$c_{n1}^{0}=c_0(n+1)^p\exp(-2nS)\ , \tag{2}$$

where S is the Huang-Rhys factor, n is the phonon number $1/[\exp(\hbar\omega/kT)-1]$, $\hbar\omega$ is the phonon energy, p is the number of phonons emitted during the cooling transition, and c_0 is considered temperature independent and equal to c_{n1}^{0} at very low temperatures. We relate p to $\hbar\omega$ by the known energy gap E_G of Si and trap depth of the second Zn acceptor level,[25] $p=(E_G-664\ \text{meV}+kT)/\hbar\omega$. kT was added to take into account the fact that the average electron is captured from above the conduction-band minimum. More detailed averaging would be inconsequential to the analysis in our present case because the level is very deep.

One may be tempted to fit data to Eq. (2) to obtain c_0, S, and $\hbar\omega$.[14] As pointed out by Burt,[58] such a procedure produces an illusion of a good fit since the magnitude and the temperature dependence of a NMP capture rate are related, i.e., c_0 is actually related to S and $\hbar\omega$ by

$$S=\left[\frac{(p-2)!c_0K^3\exp[(2n+1)S]}{16\omega\pi^2(n+1)^pR_1}\right]^{1/p}, \tag{3}$$

where the parameters $R_1=0.18$ (Ref. 14) and $K=7.7\times10^6$ cm$^-$ (Ref. 58) will be used.

Burt[58] was reluctant to use Eq. (2) and would only determine S as a function of $\hbar\omega$ from Eq. (3). We feel that this was too conservative. We will take a bold approach by making a least-squares fitting of data to Eq. (2) subject to the constraint of Eq. (3), i.e., a self-consistent least-squares fit. This results in $c_0=(1.07\pm0.04)\times10^{-9}$ cm^{3}s^{-1}, $S=1.40\pm0.26$, and $\hbar\omega=(50.4\pm1.2)$ meV. The fitted curve was also shown in Fig. 4. The use of Eq. (2) is justified since the values satisfy the condition $p^2\gg4(n+\frac{1}{2})S$.[14]

The fitted c_0 has a reasonable magnitude for a "neutral" center,[2] and is indeed close to the neutral c_{n0} at low temperature to be presented in Sec. III B. The fitted $\hbar\omega$ implies the dominance of the longitudinal-optical phonon in localized electron-phonon coupling, which has been predicted.[2,30] The S value gives a lattice relaxation energy of $S\hbar\omega\simeq70$ meV. The details of lattice relaxation in Si are not understood;[55] nevertheless, photoionization spectra of Zn (Refs. 21 and 22) can be viewed as conclusive evidence indicating the lack of a large Franck-Condon shift[55] and also indicating that a value of $S\hbar\omega$ greater than 0.1 eV would be extremely unlikely, contrary to Ridley's[30] rough estimation of 0.6 eV.

Although the fitting parameters were all reasonable, the fit as seen in Fig. 4 did not appear to describe the data exceedingly well since the deviation over the entire temperature range seemed systematic rather than random. This is not surprising since the current state of theory, as reviewed by Stoneham,[7] contains numerous simplifications that are not clearly justifiable even for a well-behaved center such as Zn in Si. For instance, Eq. (2) was derived using a single phonon frequency and one-dimensional CC diagram, but the nearest-neighbor Si atoms around the Zn center already have 12 degrees of freedom. In fact, even the basic course of the current theory has been challenged by Morgan.[59] Considering the complexity of the problem, we feel that improvements in theory would be difficult without the guidance of a catalog of properly interpreted, accurate, and reliable data, for which we hope to provide an example in this work.

Of significance in the results of the analysis just described are (i) below room temperature the electronic barrier dominates over the vibronic barrier in determining the temperature dependence of the capture rate, (ii) the NMP self-consistent fit was possible because we could obtain its true magnitude by factoring out the charge effect, and (iii) the low-temperature NMP is by tunneling through the vibronic barrier, an essentially quantum process[14,30] similar to that which happens to the electronic barrier. There is no hope of understanding the capture-

rate data below room temperature by classical or semiclassical models as previous authors have attempted.

B. Electron-capture rate c_{n0} at first acceptor level ($E_V + 326$ meV)

The original proposal by Sheinkman[10] that the carrier-capture rates associated with many centers with multiple charge states may be due to a local Auger mechanism has intrigued researchers for two decades.[3] Unlike a free-carrier Auger mechanism, capture due to a local Auger mechanism does not have the characteristic carrier-concentration dependence, and thus direct experimental means of identifying it were previously unknown.[54] A local Auger mechanism should give distinct features in photoconductivity decay;[10] however, the methods were indirect and subject to interpretation. Theoretical prediction of its magnitude proved virtually impossible at this stage,[11] due to the high sensitivity of matrix elements from the wave functions. Sheinkman's[10] suggestion that it might be identified by the relatively large magnitude contradicts the theory,[11] and, furthermore, the reliable data of hole capture at neutral Ti (Ref. 41) and neutral Au (Ref. 60) in Si, where the local Auger mechanism can be ruled out by energy conservation, all give capture rates at about 10^{-8} cm^3 s^{-1}, which was upper limit of the local Auger rate given by Sheinkman.

On the other hand, as pointed out in Sec. I, it is essential to resolve this issue for a successful recombination modeling. Not recognized previously is that the double-pulse method provides a direct test of this mechanism. The very fact that we were able to measure c_{n1} (see Fig. 1) down to 77 K proved that the local Auger effect was insignificant. In the double-pulse measurement of c_{n1} at low temperature, when a bound hole is frozen onto the first acceptor level, the electrons during the filling pulse were captured at the first acceptor level before they fill the second acceptor level. Had the local Auger mechanism been important, part or all of the trapped holes at the second acceptor level would have been ejected out, and would not have been available to capture, or recombine with, electrons. The degree of ejection of trapped holes should also have depended on the filling pulse width used to measure c_{n1}, and the filling pulse sequence, i.e., results from the double-pulse or multiple-pulse mode would have been different. None of these were observed. The size of the capacitance change corresponding to the filling of the second acceptor level was the same at low or higher temperatures, and the semilogarithmic plot of capacitance change versus filling pulse width was always an excellent straight line with a slope independent of filling pulse widths used or their sequence. These confirm the unimportance of the localized Auger mechanism.

The c_{n0} data are shown in Fig. 5. c_{n0}'s value was $(5.05\pm0.29)\times10^{-10}$ cm^3 s^{-1}, independent of temperature in the range of measurement. The magnitude is close to the plateau value of the neutral part of c_{n1} (see Fig. 4). This is too large for radiative capture; therefore, it must be due to NMP. The lack of temperature dependence of

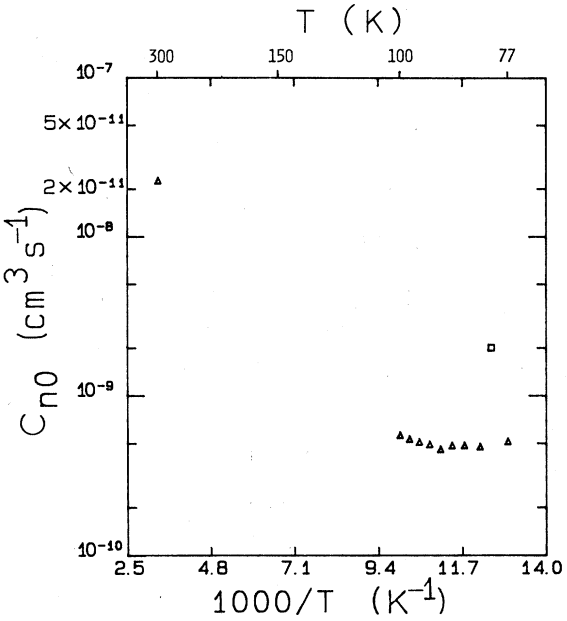

FIG. 5. Temperature dependence of c_{n0}. Triangles: zero-field data by this work, except that the point at room temperature was from Sah *et al.* (Ref. 25). Square: high-field data by Herman and Sah (Ref. 21).

c_{n0} at low temperature and its magnitude are both consistent with the fact that the capture is at a neutral center. The room-temperature value in Fig. 5 was due to an interpretation of lifetime data by Sah.[25] It indicated that c_{n0} should increase at some intermediate temperature, which was expected by NMP theory. However, the level was relatively shallow, so that its fast hole emission rate did not allow us to use the most accurate double-pulse method at higher temperatures, resulting in the data gap between 100 and 300 K. We can safely conclude that the local Auger mechanism is insignificant at all temperatures, even though this was directly proven only at lower temperatures. This is because the local Auger rate can have, at most, a moderate temperature dependence.[2,3]

Also shown for comparison in Fig. 5 was the high-field data of Herman and Sah.[21] The difference is not surprising in view of the high-field—hot-electron effect.[1,12,61] A more dramatic example of high-field effects was the 5-orders-of-magnitude enhancement by electric field at the EL2 center in GaAs observed by Prinz and Rechkunov.[61]

IV. CONCLUSIONS

We analyzed one of the simplest cases of carrier capture at deep centers, namely electron capture at the two zinc levels in silicon, and showed that our attempt is very fruitful. With the known properties of the center we were able to make a detailed analysis of the capture rate. Electron-capture rates at both zinc levels were directly and accurately measured by the capacitance transient techniques for the first time. Our analyses showed that a localized Auger mechanism is insignificant. We also

showed that the electronic barrier dominates over the vibronic barrier in determining the temperature dependence of capture rate below room temperature, and it is essentially tunneling limited. The recognition of Debye screening or curtailment of the impurity Coulomb potential has also major bearings on recombination physics. The fact that nonradiative multiphonon emission is responsible for energy dissipation during carrier capture does not mean that it controls the temperature dependence of the capture rate, as is usually implied in the literature. Overlooking these important mechanisms may result in fitted trap parameters at severe variance with the physical reality and in erroneous recombination models.

ACKNOWLEDGMENTS

This work is partially supported by the U.S. Department of Energy through the Jet Propulsion Laboratory, (California Institute of Technology), the Semiconductor Research Corporation, and the U. S. National Science Foundation. One of us (L.S.L.) is supported by a Taiwan government fellowship.

APPENDIX

The recombination parameters of zinc in silicon are summarized below in least-squares-fit equations. They follow Sah *et al.*,[25] except that the zero-field data of c_{n1} and c_{n0} from this work were used in fitting to Eq. (2) with F in Eq. (1) as a multiplier in c_{n1}.

For the second acceptor level ($E_V + 664$ meV),

$$e_{p1}=(5.36\pm0.21)\times10^{12}(300/T)^2\exp[-(664\pm1\text{ meV})/kT]\ \text{s}^{-1}\ ,$$

$$c_{n1}=(3.03\pm0.11)\times10^{-6}T^{-2/3}\exp[-(4.10\times10^5/T)^{1/3}]\{1-\exp[-(585\pm14)/T]\}^{-(9.86\pm0.23)}$$
$$\times\exp\left[\frac{-2.80\pm0.52}{\exp[(585\pm14)/T]-1}\right]\ \text{cm}^3\,\text{s}^{-1}\ ,$$

$$c_{p2}=(5.72\pm0.55)\times10^{-8}(300/T)^{3.93\pm0.15}\ \text{cm}^3\,\text{s}^{-1}\ ,$$

$$e_{n2}=n_i^2c_{n1}c_{p2}/e_{p1}\ .$$

For the first acceptor level ($E_V + 326$ meV),

$$e_{p0}=(7.41\pm0.74)\times10^{12}(300/T)\exp[-(326\pm1\text{ meV})/kT]\ \text{s}^{-1}\ ,$$

$$c_{n0}=(4.61\pm0.08)\times10^{-10}\{1-\exp[-(481\pm3)/T]\}^{-(20.1\pm0.2)}\exp\left[\frac{-2.23\pm0.21}{\exp[(481\pm3)/T]-1}\right]\ \text{cm}^3\,\text{s}\ ,$$

$$c_{p1}=(4.9\pm0.7)\times10^{-8}(300/T)^{2.15\pm0.14}\ \text{cm}^3\,\text{s}^{-1}\ ,$$

$$e_{n1}=n_i^2c_{n0}c_{p1}/e_{p0}\ .$$

[1]See, e.g., A. G. Milnes, *Deep Impurities in Semiconductors* (Wiley, New York, 1973).
[2]See, e.g, A. M. Stoneham, *Theory of Defects in Solids* (Oxford University Press, London, 1975).
[3]See, e.g., M. Jaros, *Deep Levels in Semiconductors* (Hilger, Bristol, 1982).
[4]W. Shockley and W. T. Read, Jr., Phys. Rev. **87**, 835 (1952).
[5]R. N. Hall, Phys. Rev. **87**, 387 (1952).
[6]C. T. Sah and W. Shockley, Phys. Rev. **109**, 1103 (1958).
[7]A. M. Stoneham, Rep. Prog. Phys. **44**, 79 (1981).
[8]C. T. Sah, L. Forbes, L. L. Rosier, and A. F. Tasch, Jr., Solid-State Electron. **13**, 759 (1970); C. T. Sah, *ibid.* **19**, 975 (1976).
[9]G. L. Miller, D. V. Lang, and L. C. Kimerling, Annu. Rev. Mater. Sci. **7**, 377 (1977).
[10]M. K. Sheinkman, Fiz. Tverd. Tela (Leningrad) **7**, 28 (1965) [Sov. Phys.—Solid State **7**, 18 (1965)].
[11]F. A. Riddoch and M. Jaros, J. Phys. C **13**, 6181 (1980).
[12]V. L. Bonch-Bruevich and E. G. Landsberg, Phys. Status Solidi **29**, 9 (1968).
[13]R. Paessler, Phys. Status Solidi B **78**, 625 (1976); Solid-State Electron. **27**, 155 (1984).
[14]B. K. Ridley, J. Phys. C **11**, 2323 (1978).
[15]B. K. Ridley and M. A. Amato, J. Phys. C **14**, 1224 (1981).
[16]W. Shockley, IEEE Trans. Electron Devices **ED-23**, 597 (1976).
[17]L. V. Keldysh, Zh. Eksp. Teor. Fiz. **18**, 265 (1964) [Sov. Phys.—JETP **18**, 253 (1964)].
[18]S. T. Pantelides, Rev. Mod. Phys. **50**, 797 (1978).
[19]R. G. Humphreys, J. Phys. C **14**, 2935 (1981).
[20]L. A. Ledebo, J. Phys. C **14**, 3279 (1981).
[21]J. M. Herman III and C. T. Sah, Phys. Status Solidi A **14**, 405 (1972); J. Appl. Phys. **44**, 1259 (1973); Solid-State Electron. **16**, 1133 (1973); J. M. Herman III, Ph.D. thesis, University of Illinois, 1972.
[22]A. F. Sklenski and R. H. Bube, Phys. Rev. B **6**, 1328 (1972).
[23]B. G. Cartling, J. Phys. C **8**, 3183 (1975).
[24]L. A. Hemstreet, Phys. Rev. B **15**, 834 (1977).
[25]C. T. Sah, P. C. Chan, A. C. Wang, R. L. Sah, K. A. Yamakawa, and R. Lutwack, IEEE Trans. Electron Devices **ED-28**, 304 (1981).
[26]J. Bernholc, N. O. Lipari, S. T. Pantelides, and M. Scheffler, Phys. Rev. B **26**, 5706 (1982).
[27]A. Zunger and U. Lindefelt, Phys. Rev. B **27**, 1191 (1983).
[28]F. Barra, P. Fisher, and S. Rodriguez, Phys. Rev. B **7**, 5285

(1973), and references therein.
[29]H. Nakata and E. Otsuka, Phys. Rev. B (to be published).
[30]B. K. Ridley, Solid-State Electron. **21**, 1319 (1978).
[31]See, e.g., W. R. Runyan, *Silicon Semiconductor Technology* (McGraw-Hill, New York, 1965).
[32]N. Sclar, Solid-State Electron. **24**, 203 (1981).
[33]C. T. Sah and A. Neugroschel, IEEE Trans. Electron Devices **ED-23**, 1069 (1976).
[34]T. J. Woodley and C. T. Sah, Solid-State Electron. **20**, 385 (1977).
[35]N. Sclar, IEEE Trans. Electron Devices **ED-24**, 709 (1977), and references therein.
[36]See, e.g., L. D. Landau and E. M. Lifshitz, *Quantum Mechanics,* 3rd ed. (Pergamon, Oxford, 1977).
[37]R. Bube and F. Cardon, J. Appl. Phys. **35**, 2712 (1964).
[38]G. E. Fenner, Solid-State Electron. **10**, 753 (1967).
[39]M. M. Mandurah, K. C. Saraswat, and T. I. Kamins, IEEE Trans. Electron Devices **ED-28**, 1163 (1981).
[40]R. Paessler, Phys. Status Solidi B **85**, 203 (1978); **103**, 673 (1981).
[41]A. C. Wang and C. T. Sah, J. Appl. Phys. **56**, 1021 (1984).
[42]Y. E. Pokrovskii and K. J. Svistunova, Phys. Status Solidi **33**, 517 (1969).
[43]R. Paessler, Phys. Status Solidi B **101**, K69 (1980).
[44]D. J. Robbins, J. Phys. C **13**, L1073 (1980).
[45]M. A. Amato and B. K. Ridley, J. Phys. C **13**, 2027 (1980).
[46]Y. E. Pokrovsky, in *Symposium on Radiative Recombination in Semiconductors,* proceedings of the Seventh International Conference on the Physics of Semiconductors, Paris (Dunod, Paris, 1964), p. 129.
[47]P. J. Dean, in *Physics of Semiconductors 1978,* edited by B. L. H. Wilson (IOP, Bristol, 1979), p. 1259.
[48]R. C. Enck and A. Honig, Phys. Rev. **177**, 1182 (1969), and references therein.
[49]A. A. Rogachev and S. M. Ryvkin, Fiz. Tverd. Tela (Leningrad) **6**, 3063 (1965) [Sov. Phys.—Solid State **6**, 3003 (1965)].
[50]See, e.g., S. M. Sze, *Physics of Semiconductor Devices,* 2nd ed. (Wiley, New York, 1981).
[51]B. Ricco and M. Y. Azbel, Phys. Rev. B **29**, 1970 (1984).
[52]C. T. Sah, T. H. Ning, L. L. Rosier, and L. Forbes, Solid-State Commun. **9**, 917 (1971).
[53]H. Kukimoto, C. H. Henry, and F. R. Merritt, Phys. Rev. B **7**, 2486 (1973).
[54]C. H. Henry and D.V. Lang, Phys. Rev. B **15**, 989 (1977).
[55]M. Jaros, Phys. Rev. B **16**, 3694 (1977).
[56]A. M. Stoneham, J. Phys. C **12**, 891 (1979).
[57]Z. Gu and K. Huang, Chin. J. Semicond. **5**, 6 (1984).
[58]M. G. Burt, J. Phys. C **12**, 4827 (1979); **14**, L845 (1981).
[59]T. N. Morgan, Phys. Rev. B **28**, 7141 (1983).
[60]R. H. Wu and A. R. Peaker, Solid-State Electron. **25**, 643 (1982).
[61]V. Y. Prinz and S. N. Rechkunov, Phys. Status Solidi B **118**, 159 (1983).