Theoretical model of the Au-Fe complex in silicon

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We report results for the electronic states of the substitutional-gold—interstitial-iron complex in silicon. The self-consistent-field calculations were performed by using the multiple-scattering $X\alpha$ theory within the framework of the Watson-sphere-terminated molecular-cluster method. Guided by these investigations, and also taking into consideration recent theoretical studies for the isolated gold and iron impurities, we propose a microscopic model which provides a fairly consistent interpretation for the electron paramagnetic resonance (EPR) and diode capacitance measurements taken on the Au-Fe center. An effective spin $S = \frac{1}{2}$ is assigned to the neutral charge state of the complex in agreement with EPR experiments. The model implies that the Au-Fe complex, as the isolated substitutional-gold center, has physical properties directly related to dangling-bond-like gap states. Furthermore the multiple-charge-state interpretation commonly invoked to explain the amphoteric behavior of the isolated gold impurity can explain the origin of the two deep levels observed for the complex. The suggested model is substantiated by the experimental fact that the Mott-Hubbard potential for the isolated gold and for the complex differ by only 0.11 eV.

I. INTRODUCTION

Among the impurities related to deep levels in silicon, gold is probably the most investigated under an experimental point of view due to its technological importance as a lifetime control impurity.[1-3] A basic goal of these investigations is the establishment of microscopic models for isolated gold or for gold-related centers in silicon in order to interpret the experimental data. Within this context, the amphoteric behavior of gold still remains as a controversial subject.[4-7] The problem was extensively analyzed by Lang *et al.* and it was concluded that the donor and acceptor deep levels commonly attributed to gold in silicon were not related to the same center.[4] However, recent experiments were performed that do not support this conclusion.[5,6] A reinterpretation of Lang and collaborators reported data by Feenstra and Pantelides also leads to the conclusion that the amphoteric behavior of gold is related to the same center.[7]

Despite the wealth of experimental data available for gold in silicon only recently attempts have been made to use elaborated theoretical models to describe the electronic structure of this center.[8-11] These works are restricted to the isolated impurity and include the application of a semiempirical tight-binding (TB) linear combination of atomic orbitals approach,[8] the use of the multiple-scattering (MS) $X\alpha$ theory[9,10] within the framework of the Watson-sphere-terminated molecular-cluster model,[12] and the application of the Green's-function (GF) method[11] according to the quasiband crystal-field technique.[13] All these calculations are consistent with the possibility of the well-known donor and acceptor levels attributed to gold in silicon being directly related to transitions involving a single substitutional gold atom in the positive $(0/+)$ and negative $(-/0)$ charge states, respectively. According to the GF calculations, a very good agreement between the experimental value for the Mott-

Hubbard potential and the theory is reached by assuming the on-center configuration for the gold impurity.[11] On the other hand, the TB and MS calculations yield the conclusion that the lattice distortions associated to the neutral, positive and negative charge states of the center play an important role in explaining the amphoteric behavior of gold.[8,14] The progress on the understanding of this and other related questions has been hindered by the fact that no electronic paramagnetic resonance (EPR) signal for isolated gold has ever been observed.[15] Moreover, the interpretation of the experimental data turns out to be difficult due to the well known fact that gold forms complex pairs with other impurities, such as Au-Fe, Au-Mn, Au-Cr, Au-P, Au-O, etc.[4,16,17]

Under a theoretical point of view one important result can be extracted from the MS and GF calculations: the on-center substitutional gold in silicon yields dangling-bond-like delocalized gap states with a small contribution originating from the impurity atomic d orbitals. This finding play a relevant role in describing important properties of the center such as the lack of an EPR signal,[11] the amphoteric behavior,[11,14] etc. On the other hand, as will be discussed in this paper, this information is crucial to the analysis of the experimental data taken on substitutional-gold-related complex pairs as well as to the microscopic modeling of these centers in silicon.

Contrary to the gold isolated impurity, the gold-transition-metal (TM) complexes have been detected by EPR experiments.[16-19] It is assumed for these systems that gold replaces a silicon atom at a regular lattice site and pairs to the TM impurity at the nearest tetrahedral-site interstitial (T) position.[17] In order to analyze the EPR spectra, the original Ludwig and Woodbury (LW) model has been adopted.[19-21] According to this interpretation, the observed EPR signals originate from the coupling between the angular momenta (spins) of two magnetic centers, described by the LW model, one centered on

the gold and the other on the TM impurity.[15,17,19] However, as we pointed out above, the MS and GF calculations lead to the conclusion that the gold atomic d orbitals play a minor role in determining the gap states properties, therefore the LW model does not provide a realistic description of the substitutional gold impurity.[11,14] This fact raises the necessity of performing a reinterpretation of the experimental data taken on these complexes.

In this paper we address ourselves to the problem of modeling the microscopic structure of gold-related complexes in silicon. The aim of this work is to report on the rigorous self-consistent calculations performed on the gold-iron complex pair. It has been observed that this system has some physical properties which are similar to those shown by the isolated gold center.[16] We analyze these similarities through comparison of our results for the complex with those obtained previously[9-11,14] for the single gold impurity. The calculations reported here were carried out by using the MS $X\alpha$ theory according to the same cluster model that has been recently used to study the isolated substitutional[9,10] and interstitial[14] gold impurity in silicon. The method has been currently adopted by us to investigate deep-level impurities in IV elemental[22,23] and III-V compound semiconductors.[12,24] The model is particularly suitable to investigate the Au-Fe complex pair, the use of elaborated GF-type methods to study such complex systems is still not possible. We simulate the Au-Fe complex through a 27-atom cluster, and the calculations are carried out to the self-consistent-field (SCF) limit by including all the electrons.

The paper is organized as follows: In Sec. II we review the essential features of the LW model as applied to the Au-Fe pair. In Sec. III the results of our calculations are discussed and a new microscopic model for the complex is proposed. A summary as well as our main conclusions are presented in Sec. IV.

II. CURRENT MICROSCOPIC MODEL FOR THE Au-Fe COMPLEX IN Si

Recently Kleinhenz and collaborators identified an EPR spectrum which was assigned to substitutional-gold—interstitial-iron-complex pair in silicon.[17] It was found that this paramagnetic center can effectively be described by a spin Hamiltonian with a single spin $S = \frac{1}{2}$. In order to interpret the data, Sieverts et al. proposed a microscopic model for the complex by assuming that the isolated gold and iron impurities are described by the LW model.[15] Moreover, as gold is more electronegative than iron [$\chi(\text{Au}) = 2.4$ and $\chi(\text{Fe}) = 1.8$ in Pauling's scale], it is assumed that there is a charge transfer of one electron from iron to gold. Accordingly, a substitutional negative gold ion would have a total spin $S = 1$ and a T-site positive iron ion a total spin $S = \frac{3}{2}$. Assuming a strong antiferromagnetic coupling between the two spins the authors conclude that the EPR spectrum can be assigned to the Si:$\text{Au}_s^-\text{Fe}_i^+$ complex with a total effective spin $S = \frac{1}{2}$. In Fig. 1, the microscopic model proposed by Sieverts et al. for the Au-Fe complex in silicon is schematically shown.[15]

In the last few years considerable progress has been made on the theoretical understanding of the electronic structure of TM impurities in semiconductors.[8-14,25-34] Rigorous calculations performed through several methods have established the roles played by the impurity atomic d orbitals in determining the properties of the centers. At present it is well known that the TM elements from the IB group when placed at the lattice substitutional site give rise to dangling-bond-like gap states.[9-12,25-27] The metal atomic d orbitals are split by the crystal field into a twofold (e) and a threefold (t_2) degenerate states which appear as resonant states within the valence band or as hyperdeep states below it. On the other hand, it is well established that the T-site iron impurity in silicon produces two levels, t_2 and e, within the band gap, with a strong contribution from the metal d states.[26,27,29]

Thus, the calculations do not support the assumptions inherent to the model discussed in this section for the Au-Fe pair complex. Indeed, the results indicate that the starting point to analyze the electronic structure of the pair is the interaction between a delocalized dangling-bond-like state related to gold and states with strong contribution from the iron $3d$ orbitals.

III. NEW MODEL FOR THE Au-Fe COMPLEX IN Si

A. Results of the calculations

The calculations reported here were performed by adopting initially a 26Si-atom cluster model in order to define the band edge of the perfect silicon crystal. This model has been analyzed previously[22] and applied to electronic state calculations of T-site interstitial gold impurity in silicon.[14] In order to simulate the Au-Fe complex an iron atom is placed at the center of the cluster (T site) and a gold atom replaces a nearest-neighbor silicon atom. The cluster is schematically shown in Fig. 2. The atoms in the cluster are classified according to four shells in T_d symmetry indicated by the numbers 1, 2, 3, and 4. The replacement of a nearest-neighbor silicon atom by gold lowers the symmetry to C_{3v} and each one of these shells are further divided in classes of equivalence denoted by a, b, and c. Thus, the cluster model comprises the central atom (Fe), the classes $1a$ (1 Au), $1b$ (3 Si), $2a$ (3 Si), $2b$ (3 Si), $3a$ (1 Si), $3b$ (3 Si), $4a$ (6 Si), $4b$ (3 Si), and $4c$ (3 Si).
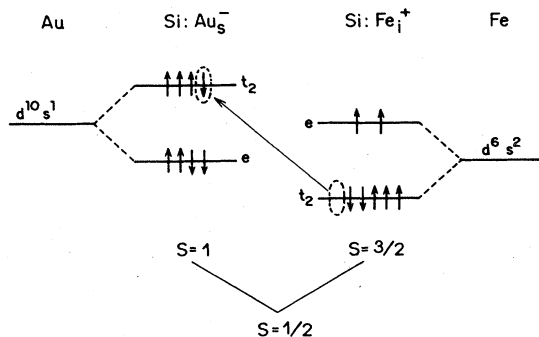

FIG. 1. Schematic representation of the Ludwig and Woodbury model as applied to the gold-iron pair complex in silicon. The strong antiferromagnetic coupling between the spins of Au_s^- ($S = 1$) and Fe_i^+ ($S = \frac{3}{2}$) yields the observed effective spin $S = \frac{1}{2}$ (after Sieverts et al., Ref. 15).

● IRON ◉ GOLD ○ SILICON

FIG. 2. Schematic representation of the 25Si + Au_sFe_i cluster simulating the Au-Fe pair complex in silicon. As a T-centered cluster it comprises one central iron atom and four shells of silicon atoms, numbered from 1 to 4, in T_d symmetry. By replacing a nearest-neighbor silicon atom by gold the cluster symmetry is lowered to C_{3v}. The atoms in this symmetry belong to classes of equivalence which are indicated by the labels a, b, and c.

FIG. 3. One-electron self-consistent energy spectra of the 26Si and 25Si + Au_sFe_i clusters simulating the electronic structure of the silicon crystal and the Au-Fe complex, respectively. The experimental values for the silicon valence-band width and band gap are also shown. The zero of energy is placed at the top of the valence band and the solid circle indicates the occupancy of the highest occupied level in the spectra.

Since the Watson-sphere-terminated cluster model is well documented,[12,22] no details about the calculations will be provided here.

The one-electron energy spectrum of the 25Si + Au_sFe_i cluster simulating the Au-Fe complex is shown in Fig. 3. We are also including in the figure the spectrum of the 26Si-atom cluster obtained previously[22] as well as the experimental values for the silicon valence-band width and indirect band gap.[35,36] According to the results obtained for the complex, the gold $5d$ atomic orbitals give rise to sharp resonances and a hyperdeep level close to the bottom of the valence band. On the other hand, we observe that just below the top of the valence band there is a set of resonant states with strong contribution from the iron $3d$ atomic orbitals. They originate from hybridization between the $3d$ orbitals of iron and the $3p$ silicon orbitals. Another important result of the calculations is that the Au-Fe pair complex in silicon gives rise to four one-electron energy eigenvalues within the band gap, three of them with strong contributions from the iron $3d$ atomic orbitals. The highest gap level, occupied by one electron, is highly delocalized showing a dangling-bond-like character. Since these levels are of fundamental importance within the context of building a microscopic model for the complex we analyze them in more detail.

In Fig. 4, the energy spectrum of the 25Si + Au_sFe_i cluster is shown in an enlarged scale. Included in the figure are only the one-electron states which are derived from gold $5d$ or iron $3d$ atomic orbitals as well as the highest $9e$ and $5a_1$ levels. The percentage of charge, normalized to one electron, within the Au or Fe atomic sphere (radius 2.22 a.u.), are shown in parentheses. In order to fully characterize these states we show in Table I the charge distribution associated to them for the different regions of the cluster. The charge within each shell is computed by multiplying the contribution from a silicon atomic sphere (radius 2.22 a.u.) by the number of equivalent atoms in the shell. According to Fig. 4, the $1a_1$ and $2e$ resonant states have the highest contribution from the gold atomic orbitals. The entries in Table I show that they are strongly localized states with 77% and 84% of charge within the gold impurity sphere, respectively. These two levels originate from the splitting of the $t_2(d)$ level obtained for the substitutional-gold impurity[9,10] due to the presence of the iron atom which lowers the crystal-field symmetry from T_d to C_{3v}. It is interesting to point out that the charge inside the gold impurity sphere for the $t_2(d)$ level found previously[9,10] is 81%. Thus, the perturbation caused by the interstitial iron atom on the gold $t_2(d)$ states is small, and they consequently remain highly localized. Although the substitutional-gold $e(d)$-derived states are somewhat more perturbed by the interaction with the iron atom, they still remain quite localized, appearing as resonances in the lower half on the valence band.

We compare now the calculations for the Au-Fe complex with those carried out for the isolated T-site iron impurity.[26,27] It has been found that the iron impurity gives rise to $3d$-derived resonant states in the upper region of the valence band, as well as introduce two energy levels, t_2 and e, in the band gap with strong contributions from the
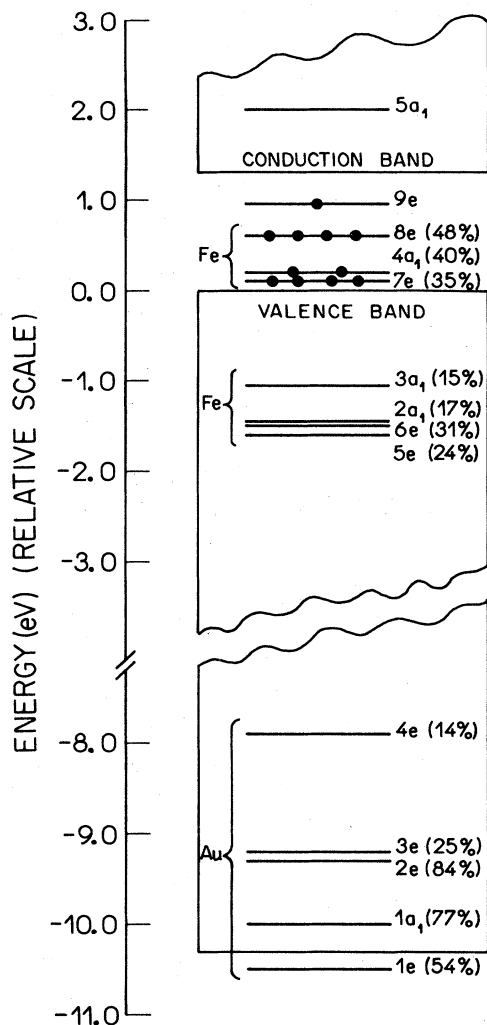
FIG. 4. Gold $5d$- and iron $3d$-derived energy levels, relative to the band edges, identified in the energy spectrum of the 25Si + Au$_s$Fe$_i$ cluster. The occupancy of the gap levels is indicated by solid circles and the values in parenthesis give the percentage of charge, normalized to one electron, within the gold or iron atomic sphere. The $9e$ and $5a_1$ are dangling-bond-like levels.

metal d states. The results shown in Fig. 4 and in Table I indicate that the overall features of the interstitial iron $3d$-derived states are not strongly changed by the interaction with gold. Iron $3d$-derived a_1 and e resonances are still found in the upper part of the valence band and there are gap states which have strong contributions from iron $3d$ atomic orbitals. The gap levels, which appear according to the $7e^4 4a_1^2 8e^4$ electronic configuration, result from the crystal-field splitting of the iron $3d$-derived $t_2 + e$ levels when the symmetry is lowered from T_d for T-site iron to C_{3v} for the Au-Fe complex.

One of the most interesting features of our calculations is the fact that the highest gap level ($9e$) is not d-like at all, but is rather mostly dangling-bond-like. It is derived from the substitutional gold t_2 gap level which splits in C_{3v} symmetry into e and a_1 levels, the latter appearing as a resonance within the continuum of the conduction band

at $E_v + 2.03$ eV. It is now worth comparing the charge distribution of the $9e$ state with the result obtained for the substitutional gold t_2 gap state.[9,10] According to the 17-atom cluster calculations for the substitutional-gold impurity the t_2 gap level, occupied by three electrons, is quite delocalized, with 4%, 27%, and 46% of charge inside the gold impurity sphere, first and second shell of silicon neighbors, respectively. The entries in Table I for the $9e$ state show that there is only 2% of charge inside the gold impurity sphere, 14% within the iron sphere, 17% and 31% inside the $2a$ and $4a$ shells, respectively. These results indicate, according to Fig. 2, that the charge for the $9e$ state is distributed on the nearest and next-nearest neighbors of the gold impurity. Thus the $9e$ gap state for the Au-Fe complex and the t_2 gap state for substitutional gold have quite analogous dangling-bond-like nature. This finding provides an explanation for the similarities observed between some properties of these centers.[16] We will return to this subject later.

Another important information that can be extracted from the calculations is the total electronic charge inside the impurity spheres. The values $77.55e$ and $26.36e$ are found for the gold and iron spheres, respectively. These results are an indication that the $Au_s^- Fe_i^+$ notation for the complex is misleading, since there is no indication of transfer of one electron from iron to gold. It is worth to point out that the differences between electronegativities of the elements do not provide a reliable criterium to analyze charge-transfer effects which take place for impurities in covalent semiconductors. The charge redistribution that follows the introduction of the impurity in the solid involves, besides other impurities in the case of a complex, the lattice host atoms. In other words, the impurities interact with the crystal valence-band states.

B. Dangling-bond-like model for the Au-Fe complex

Based on the calculations reported on the preceding section we are now at a position to describe the formation of the impurity states of the Au-Fe complex from the molecular orbitals of the isolated impurities. The model is schematically shown in Fig. 5. The t_2 dangling-bond-like level induced by the substitutional-gold impurity in T_d symmetry (Refs. 9–11) splits into the gap level $9e$ and the resonance $5a_1$ for the complex in C_{3v} symmetry. The t_2 and e impurity levels introduced in the band gap by the T-site iron impurity (Refs. 26 and 27) give rise to the fully occupied $7e$, $4a_1$, and $8e$ levels in the gap for the complex. Two main ideas are built in the model schematically shown in Fig. 5: first, the gold $5d$ states are fully occupied and strongly localized, therefore cannot interact magnetically with the iron impurity; second, the highest level for the complex is quite localized with a dangling-bond-like character. Therefore, the model proposed to interpret the EPR experiments for the complex, discussed in Sec. II of this paper, does not describe realistically the data. In order to fulfill partially the requirements of the model proposed by Sieverts *et al.* the impurities in the C_{3v} crystal-field symmetry are expected to have the $Au^-(5a_1^2 9e^2)$ and $Fe^+(4a_1^1 8e^2)$ configurations, with spins $S = 1$ and $S = \frac{3}{2}$, respectively.[15] According to the results

TABLE I. Charge distribution normalized to one electron for the iron and gold d-derived states. The orbitals are labeled as in Fig. 4. The charge for the silicon atoms are distributed into eight shells as indicated in Fig. 2. The results for the $9e$ gap state are also shown.

Orbital (occupancy)	Fe central	Au $1a$	Shell $1b$	Shell $2a$	Shell $2b$	Shell $3a$	Shell $3b$	Shell $4a$	Shell $4b$	Shell $4c$	Interatomic region
Au states
$1e(4)$	0.01	0.54	0.06	0.26	0.01	0.00	0.00	0.00	0.00	0.00	0.12
$1a_1(2)$	0.02	0.77	0.04	0.03	0.04	0.01	0.00	0.00	0.00	0.00	0.09
$2e(4)$	0.00	0.84	0.05	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.08
$3e(4)$	0.02	0.25	0.33	0.03	0.20	0.00	0.00	0.00	0.00	0.00	0.16
$4e(4)$	0.01	0.14	0.07	0.25	0.34	0.00	0.00	0.02	0.01	0.01	0.17
Fe states
$5e(4)$	0.24	0.00	0.24	0.17	0.02	0.00	0.06	0.07	0.00	0.00	0.19
$6e(4)$	0.31	0.00	0.20	0.06	0.12	0.00	0.04	0.02	0.05	0.02	0.18
$2a_1(2)$	0.17	0.02	0.17	0.15	0.12	0.00	0.02	0.02	0.11	0.00	0.22
$3a_1(2)$	0.15	0.06	0.06	0.23	0.05	0.01	0.03	0.17	0.03	0.01	0.22
$7e(4)$	0.35	0.03	0.09	0.12	0.09	0.00	0.04	0.06	0.02	0.04	0.16
$4a_1(2)$	0.40	0.03	0.02	0.07	0.01	0.26	0.03	0.00	0.00	0.01	0.17
$8e(4)$	0.48	0.00	0.08	0.04	0.06	0.00	0.09	0.06	0.04	0.04	0.12
Dangling-bond-like gap state
$9e(1)$	0.14	0.02	0.05	0.17	0.01	0.00	0.12	0.31	0.01	0.00	0.19

schematically shown in Fig. 5 no such configurations seem to be likely. Moreover, we observe also that there is no possibility for $S = \frac{3}{2}$ on neutral Au or $S = 1$ on neutral Fe.

We search now for the possible values for the total spin of the neutral Au-Fe complex, keeping in mind that this observable does not result from the coupling between the angular momenta of two magnetic centers but is rather related to the complex molecular orbitals which are spread out over the entire cluster. The most likely configurations are shown in Fig. 6. The energy levels in the gap are labeled according to Figs. 4 and 5 and the "up" ($+$) and "down" ($-$) spins are indicated. The gap level $7e$, which remains fully occupied is not shown. Three configurations shown in Fig. 6 present high spin ($S = \frac{3}{2}$) and one presents low spin ($S = \frac{1}{2}$). In the open shell configura-

tions (a), (b), and (d) the complex is unstable with respect to Jahn-Teller (JT) distortions. In configuration (c) no JT instabilities are expected to occur.

Although the calculations were not carried out to the spin-polarized limit and distortions were not taken into account, it is possible to infer that configuration (d) is the most probable one for the complex. According to our results the energy difference between the $9e$ dangling-bond-like level and the $8e$ iron $3d$-like level is 0.37 eV. In order for the configurations (a) or (b) to occur it is required that the exchange splitting of the $8e$ level be such that the $8e^-$ level lies above the $9e^+$ or above the $9e^-$, respectively. Despite the high $3d$ atomic orbital contributions for the $8e$ states, we do not expect the exchange splitting of this level to be larger than 0.37 eV.[29] Thus, we consider configurations (a) and (b) unlikely. The same statement is valid as far as the (c) configuration is concerned. In order to have the $4a_1^-$ level above the $9e^-$, an exchange splitting of about 0.7 eV is expected for the iron $3d$-derived gap levels. These considerations lead to the conclusion that configuration (d) for the neutral charge state of the Au-Fe complex is highly likely to occur. Since the unpaired electron is occupying a delocalized state the angular momentum is quenched[11] and the effective spin of the
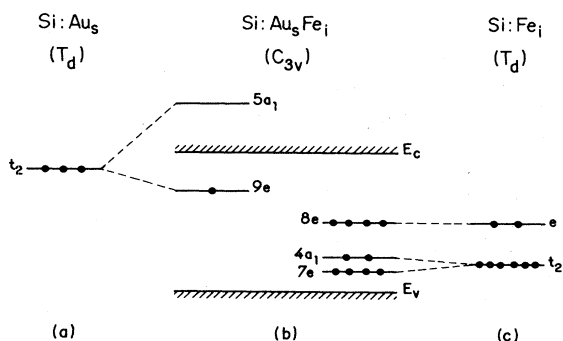

FIG. 5. Schematic representation of the impurity levels of the Au-Fe complex in silicon as originated from the interaction between molecular orbitals of the isolated impurities. The band edges are indicated and the full circles represent the occupancy of the levels. (a), (b), and (c) indicate the one-electron impurity levels for substitutional gold, for the Au-Fe complex, and for the T-site iron, respectively. The levels for the complex are labeled according to Fig. 4.
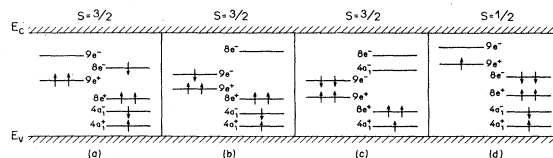

FIG. 6. Possible electronic configurations for the gap levels of the Au-Fe complex in silicon. The levels are labeled according to Figs. 4 and 5 and the $7e$ gap level is not shown. The "up" and "down" spins are indicated by the $+$ and $-$ marks, respectively. The total spin S for each configuration is also given.

complex turns out to be the $S = \frac{1}{2}$. It is worth mentioning that the same low-spin configuration ($S = \frac{1}{2}$) has been proposed for the neutral substitutional isolated gold impurity in silicon.[11]

Two deep levels at $E_c - 0.354$ eV and $E_v + 0.434$ eV have been ascribed to the Au-Fe complex in silicon according to combined EPR and diode capacitance measurements.[16] It is interesting to compare them with those attributed to isolated gold, an acceptor at $E_c - 0.55$ eV, and a donor at $E_v + 0.35$ eV.[3,4] As has been already pointed out, recent calculations[7-11] and experiments[5,6] reinforce the conventional multiple-charge-state interpretation for the acceptor and donor levels of gold in silicon. If we now take into consideration the strong similarities between the t_2 gap state for isolated gold and the $9e$ gap state for the complex we can invoke the same multicharge state model to attribute the two deep levels related to the complex to the same center. Accordingly, the first donor transition $(0/+)$ at $E_v + 0.434$ eV corresponds to the ionization of a single electron in the $9e$ level. The first acceptor level $(-/0)$ at $E_c - 0.354$ eV corresponds to the capture of one electron resulting in a double occupancy of the $9e$ state. The conventional multiple-charge-state model for the gold center as well as the same model as applied to the Au-Fe complex are schematically shown in Fig. 7. The value of the Mott-Hubbard potential U for each system is extracted from the experimental results and shown in the figure. The fact that these potentials differ by only 0.11 eV can be regarded as supporting evidence of the strong similarity between the gold dangling-bond-like t_2 gap states and the $9e$ gap states for the Au-Fe complex.

According to EPR experiments for the complex, in n-doped material as well as in p-doped material, the signal was only observed in the samples under illumination. These experiments suggest that the two deep levels observed are of the same Au-Fe center;[16] therefore they support our multicharge-state interpretation for the complex. The EPR signal, which has been associated with the neutral-charge state of the defect,[16] indicates a (111) trigonal symmetry (C_{3v}) for the center.[17] The spectrum depicted in Fig. 4 and reproduced in Fig. 5 shows that the neutral ground state of the complex is a ^2E multiplet state.

Although this result indicates that the defect is an active JT center, we conclude that in order to match the EPR results the distortions are expected to be small or absent.[37] The final state of the donor transition is a symmetric ^1A state. The one-electron final state of the acceptor transition, which has the $9e^2$ configuration, can also be JT active and would be affected by many-electrons effects.[28] However, as has been discussed in Ref. 11 for the gold impurity, the multiplet corrections are expected to be small due to the delocalized character of the $9e$ dangling-bond-like states.[28] On the other hand, the second donor transition $(+/2+)$ for the complex involves a final state with strong iron $3d$ localized atomic character. In this case the multiplet corrections must be included in the calculations in order to realistically describe the final state.[28]

IV. SUMMARY AND CONCLUSIONS

Based on the results obtained in this work as well as on the conclusions reached from previous calculations[9-11,26,27] we propose a microscopic model to describe the electronic structure of the substitutional-gold—interstitial-iron complex pair in silicon. The model provides a fairly good explanation for the EPR and diode capacitance measurements taken on a gold-related center in silicon ascribed to the Au_sFe_i complex.[16-19] It also explains the similarities observed between this center and the isolated substitutional-gold impurity in silicon.[16]

The model was built based upon the demonstration that the relevant electrical, optical, and magnetic properties of the substitutional-gold—interstitial-iron complex pair in silicon are directly related to dangling-bond-like states. It is verified that the gold $5d$- as well as the iron $3d$-derived states play a minor role in determining these properties. We found that the neutral complex ground state ^2E has an effective spin $S = \frac{1}{2}$ which results from a single occupancy of a delocalized state. According to the model the $S = \frac{1}{2}$ spin of the center, which is observed by EPR, is related to a molecular orbital spread out over the entire cluster rather than being derived from the interactions between two localized magnetic centers as has been proposed.[15] The similarities between the isolated substitutional-gold impurity and the complex lead to the conclusion that the conventional multicharge-state model is also applicable to the latter. Thus, we assume that there are two deep levels associated with the Au-Fe complex corresponding to transitions involving three charge states: a donor level, related to a single-electron ionization $(0/+)$ from the complex ^2E ground state; an acceptor level related to the capture of one electron $(-/0)$ in this state. These donor-acceptor activities, as for the isolated gold center, involve quite delocalized impurity states. The conclusions mentioned above provide an explanation for the origin of the two deep levels observed for the complex.[16,38,39]

We now analyze the results obtained by applying the microscopic model proposed here for the Au-Fe complex to gold-related centers formed by pairing with other interstitial $3d$-TM impurities. Previous calculations indicate that for Cu, Ni, and Co, the $3d$-derived one-electron energy levels are deeper than the corresponding ones for
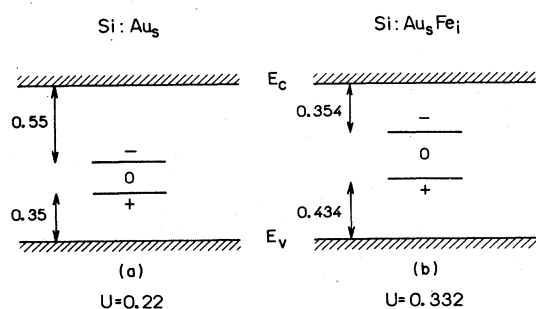

FIG. 7. (a) Conventional multiple-charge-state model used to describe the experimental values for the gold donor $(0/+)$ and acceptor $(-/0)$ levels in silicon. (b) The same model as used to interpret the two observed deep levels ascribed to the Au-Fe complex. U indicates the Mott-Hubbard potential for each system. All energies are in eV.

Fe.[26,27] Thus the model remains valid and the starting point to understand the electronic properties of the complexes are the dangling-bond-like gap states according to the configurations $9e^4$ ($S=0$), $9e^3$ ($S=\frac{1}{2}$), and $9e^2$ ($S=1$ or 0) for Si:Au_sCu_i, Si:Au_sNi_i, and Si:Au_sCo_i, respectively. However, for Mn and Cr the $3d$-derived states are higher in energy when compared with Fe;[26,27] therefore configurations (a) and (b), shown schematically in Fig. 6, may occur.

It has been argued based on theoretical works that the substitutional-gold impurity in silicon gives rise to deep states in the gap which are due to the broken bonds on the silicon neighbors.[40] In other words they are vacancy-like states [9,10,27] Taking this "vacancy" model into considera-

tion the tendency of gold to form complexes by pairing with other impurities can be understood. In the particular case of the Si:Au_sFe$_i$ complex analyzed here we are bearing in mind when constructing the microscopic model of the center that its electronic properties are directly related to vacancy-like gap states.

ACKNOWLEDGMENTS

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[40] According to the GF calculations reported in Ref. 11 there is a small contribution for these states from gold $5d$ atomic orbitals. The authors refer to these gap states as "dangling-bond hybrids" (DBH). It is also pointed out that, contrary to the vacancy states, the DBH have a node close to the surface of the central impurity sphere.