

Watson-sphere-terminated model applied to the Au^0 and Pt^- substitutional impurities in silicon

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The Watson-sphere-terminated cluster model within the framework of the multiple-scattering $X\alpha$ method is used to carry out electronic-structure calculations for Au^0 and Pt^- substitutional impurities in silicon. The results are related to the "vacancy" model recently proposed to describe the properties of the elements at the end of the transition-metal series.

Gold as a deep level impurity in silicon has practical importance as a lifetime controller and has been the subject of extensive study.¹⁻³ The main levels attributed to gold in silicon are an acceptor at $E_c - 0.5$ eV seen in n -type Si and a donor at $E_v + 0.35$ eV seen in p -type Si, both not being related to the same center.^{4,5} The generally accepted substitutional Au defect seems to be an appropriate model for a single gold impurity in silicon.⁶ The EPR on isolated gold in silicon has been reported only recently by Höhne⁷ who interpreted the spectrum he called Au(1) as corresponding to interstitial gold. However, Kleinhez *et al.*⁸ claim that the spectrum they called A23, interpreted tentatively as an [Au-Fe] complex, is the same as the A(1) reported by Höhne.

Another impurity that is considered a practical candidate for lifetime control in silicon is platinum, which is much less studied than gold.^{1,3} The main levels that appear to be involved are an acceptor at $E_c - 0.23$ eV in n -type Si and a donor at $E_v + 0.32$ eV in p -type Si. An acceptor at $E_v + 0.42$ eV is also reported.³ EPR was first observed for platinum in silicon by Ludwig and Woodbury.⁹ The dominant spectrum displayed C_{2v} symmetry which they interpreted as arising from an isolated single substitutional Pt^- ion which had distorted spontaneously off center in a $\langle 100 \rangle$ direction and had a spin $S = \frac{1}{2}$. Recently, Henning and Egelmeers¹⁰ have proposed that the EPR spectrum arises from a Pt-Pt pair in which a second interstitial Pt^0 atom lies near the substitutional Pt^- ion.

However, Milligan *et al.*¹¹ have observed that the structure noted by Henning and Egelmeers, seen as the shoulders on each of the main lines of the spectrum, is insensitive to the ¹⁹⁵Pt abundance in the sample and, therefore, does not arise from a hyperfine interaction with a second nearby Pt atom. Based on this observation and preliminary static stress measurements, they concluded that the original model of an isolated substitutional Pt^- ion, as given by Ludwig and Woodbury,⁹ is correct and that the character of the resonance remains as confirmatory evidence of the "vacancy" model proposed by Watkins¹² for substitutional transition elements. This proposal was deduced from the results of theoretical calculations¹³⁻¹⁵ and supposed to be generally applicable to the substitutional transition elements near the end of each series ($\text{Cu}^0, \text{Ni}^-; \text{Ag}^0, \text{Pd}^-; \text{Au}^0, \text{Pt}^-$). According to this model an on-center ion has a filled d^{10} shell and the remaining electrons occupy orbitals of t_2 symmetry located primarily on the four nearest silicon neighbors. The structure can be thought of as a closed d^{10} ion in a negative-

ly charged lattice vacancy V^- . In this way the electronic properties are expected to be very similar to those of V^- which has spin $S = \frac{1}{2}$ and also displays a large $\langle 100 \rangle$ static dihedral Jahn-Teller distortion resulting from the degeneracy of its partially filled t_2 states.

In this work we report rigorous calculations of the electronic structure of substitutional Au^0 and Pt^- in silicon. To our knowledge the only calculations reported before were those performed by Lowther¹⁶ for Au in silicon using a semiempirical tight binding linear combination of atomic orbitals (LCAO) approach. We use a localized description of the defect by means of the "Watson sphere terminated cluster" model developed by Fazzio and co-workers.^{17,18} This model utilizes the self-consistent multiple-scattering $X\alpha$ formalism (MS- $X\alpha$) (Ref. 19) within the framework of the standard muffin-tin potential approximation and presents a suitable treatment of the cluster surface orbitals. This model has been already applied successfully to the study of

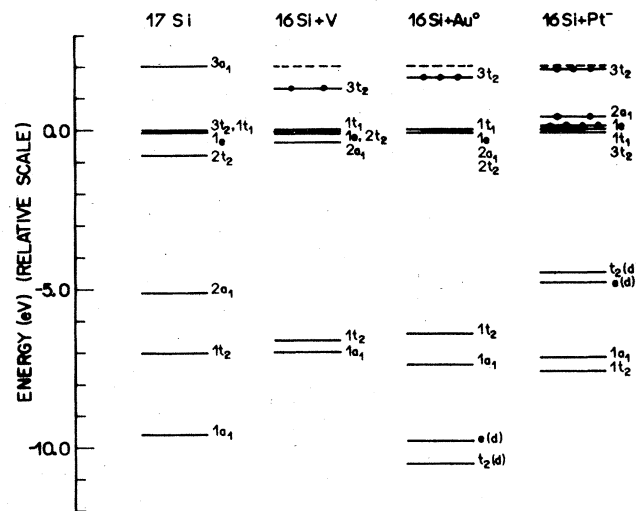


FIG. 1. Energy spectra of the clusters 17 Si, 16 Si+V, 16 Si+Au⁰, 16 Si+Pt⁻. The uppermost occupied level ($3t_2$) in the energy spectrum of the 17 Si cluster representing the ideal crystal was placed at the zero of energy. The $1t_1$ level is essentially a bulk valence energy level in the "perfect" and "defect" clusters and is taken as reference to energy scale. The dashed lines denote the bottom of the conduction band. The full circles indicate the occupancy of the gap levels.

TABLE I. Charge distribution normalized to one electron for the e and t_2 levels of the "defect" clusters. The orbitals are labeled as in Fig. 1.

Impurity	Orbital	Central atom	First shell	Second shell	Interatomic region
Au ⁰	$e(d)$	0.93	0.00	0.00	0.07
	$1e$	0.00	0.27	0.47	0.26
	$t_2(d)$	0.81	0.11	0.00	0.08
	$1t_2$	0.10	0.65	0.07	0.18
	$2t_2$	0.00	0.27	0.46	0.27
Pt ⁻	$e(d)$	0.89	0.01	0.02	0.08
	$1e$	0.02	0.25	0.48	0.25
	$t_2(d)$	0.61	0.22	0.04	0.13
	$1t_2$	0.22	0.57	0.04	0.17
	$2t_2$	0.01	0.26	0.47	0.26

defects in IV and III-V tetrahedrally coordinated semiconductors.²⁰⁻²⁴

The "defect" cluster model used consists of a central impurity atom surrounded by 16 Si atoms (4 first neighbors and 12 second neighbors) in a tetrahedral configuration compatible with the undistorted Si lattice geometry; the muffin-tin atomic spheres were chosen so as to touch each other having the same radii consistent with the silicon lattice constant 5.431 Å. The sphere which surrounds the whole cluster touches the cluster surface atomic spheres and is coincident with the Watson sphere.²⁵ The exchange parameters α utilized were 0.72751 for Si and 0.66666 for Au and Pt.^{26,27} We used the value $\alpha=0.72393$ for the interatomic region and $\alpha=0.72751$ for the outer region. The inner atomic shells up to $4f$ in Au and Pt and up to $2p$ in Si were kept frozen as in the free atoms. The basis set for the expansion of the wave functions included $l=0, 1$, and 2 for Au, Pt, and the outer region and $l=0, 1$ for Si.

In Fig. 1 we compare the energy spectra obtained from the self-consistent calculations for the "perfect" 17 Si cluster, the neutral vacancy cluster¹⁸ which has a missing central atom, and the "defect" 16 Si + Au⁰ and 16 Si + Pt⁻ clusters.

We start analyzing the results we obtained for gold. According to our calculations the $e(d)$ and $t_2(d)$ levels which are of " d " character (see Table I) lie 0.26 and 0.96 eV below the valence band, respectively. The $5d$ levels of gold in silicon behave as atomic, the electrons interacting very weakly with the lattice; this behavior is similar to that predicted by the calculations of Cartling¹³ for zinc in silicon, by Hemstreet¹⁴ for copper in silicon, and by Fazzio and Leite²⁰ for copper in GaAs.

Another important feature is that the impurity introduces a sixfold degenerate t_2 level in the band gap. As observed by Hemstreet¹⁴ in the case of copper impurity, the t_2 levels in the gap are not d like at all, but rather mostly dangling-bond-like on the four silicon neighbors (Table II).

The almost identical energy spectra (Fig. 1) and charge

TABLE II. Charge distribution normalized to one electron for the gap states of the vacancy, Au⁰ and Pt⁻.

	$3t_2(V)$	$3t_2(\text{Au}^0)$	$3t_2(\text{Pt}^-)$	$2a_1(\text{Pt}^-)$	$1e(\text{Pt}^-)$
Central atom	0.03	0.04	0.05	0.08	0.02
First shell	0.28	0.27	0.18	0.40	0.25
Second shell	0.46	0.46	0.55	0.24	0.48
Interatomic region	0.22	0.22	0.21	0.28	0.25

distribution (Table II) for Au⁰ and the vacancy are also apparent, except for the addition of a completely filled d^{10} shell.

This result confirms the "vacancy" model proposed by Watkins.¹² The Au⁰ center behaves basically as a "perturbed" silicon vacancy with a filled derived atomic d level localized below the bottom of the crystal valence band.

We turn now to the analysis of the Pt⁻ center which has some special features as compared to the Au⁰ center. First of all, the $e(d)$ and $t_2(d)$ levels lie in the middle of the valence band (Fig. 1). The $t_2(d)$ level has a strong overlap with the ligand vacancy $1t_2$ orbitals (Table I) and forces the t_2 gap level of the vacancy to move up in energy and to come near to the conduction band. While in the case of the $3d$ transition elements similar calculations¹³⁻¹⁵ show that there is either a dangling-bond t_2 gap level or an e occupied gap state, but not both; in the Pt⁻ case one has not only the $3t_2$ level but also the $1e$ and $2a_1$ levels introduced in the band gap. A similar result was obtained by Fazzio and Leite²⁰ for iron substitutional impurity in GaAs. The impurity states $3t_2$, $1e$, and $2a_1$ are rather delocalized states with a significant fraction reaching the next-nearest-neighbor shell (Table II). The energy level $1e$ is located close to the top of the valence band and has negligible contribution from platinum d states. Similarly, the $2a_1$ level has strong contributions only from silicon s and p orbitals.

On the other hand, although the Pt⁻ center does not behave exactly as a "perturbed" silicon vacancy, its half-occupied $3t_2$ level has a similar charge distribution as the vacancy $3t_2$ level and still may justify the dihedral distortion and spin $S=\frac{1}{2}$ detected for this center, as argued by Watkins in his "vacancy" model.

Based on the results for platinum impurity which lies near the end of the $5d$ series one can expect interesting features of the gap levels introduced by the other lighter members of the series. Calculations in this direction are underway.

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