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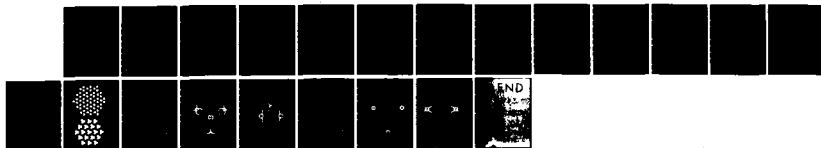
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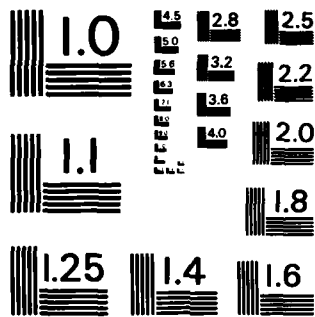
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 8	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Electronic Structure, Chemical Bonding, and Electron Conductivity of Thin-Film Transition- Metal Silicides		5. TYPE OF REPORT & PERIOD COVERED Interim
7. AUTHOR(s) K. H. Johnson and F. A. Leon		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Center for Materials Science and Engineering, M.I.T., Cambridge, Massachusetts 02139		8. CONTRACT OR GRANT NUMBER(s) N00014-81-K-0499
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Task No. Nr 056-757
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE September 10, 1984
		13. NUMBER OF PAGES 7
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approval for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Prepared for Publication in Solid State Communications		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) electronic structure chemical bonding electron conductivity thin-film transition-metal silicides		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The local electronic densities of states and chemical bonding of thin-film palladium and molybdenum silicides are compared on the basis of embedded cluster molecular-orbital calculations. Composite Pd(d)-Si(p)antibonding/Si(p)-Si(p)bonding character and composite Mo(d)-Si(p)nonbonding/Mo(d)-Si(d)bonding character at the respective Fermi energies are responsible for the different electrical conductivities of these silicide films and for the different Schottky barriers of the corresponding silicide/silicon systems.		

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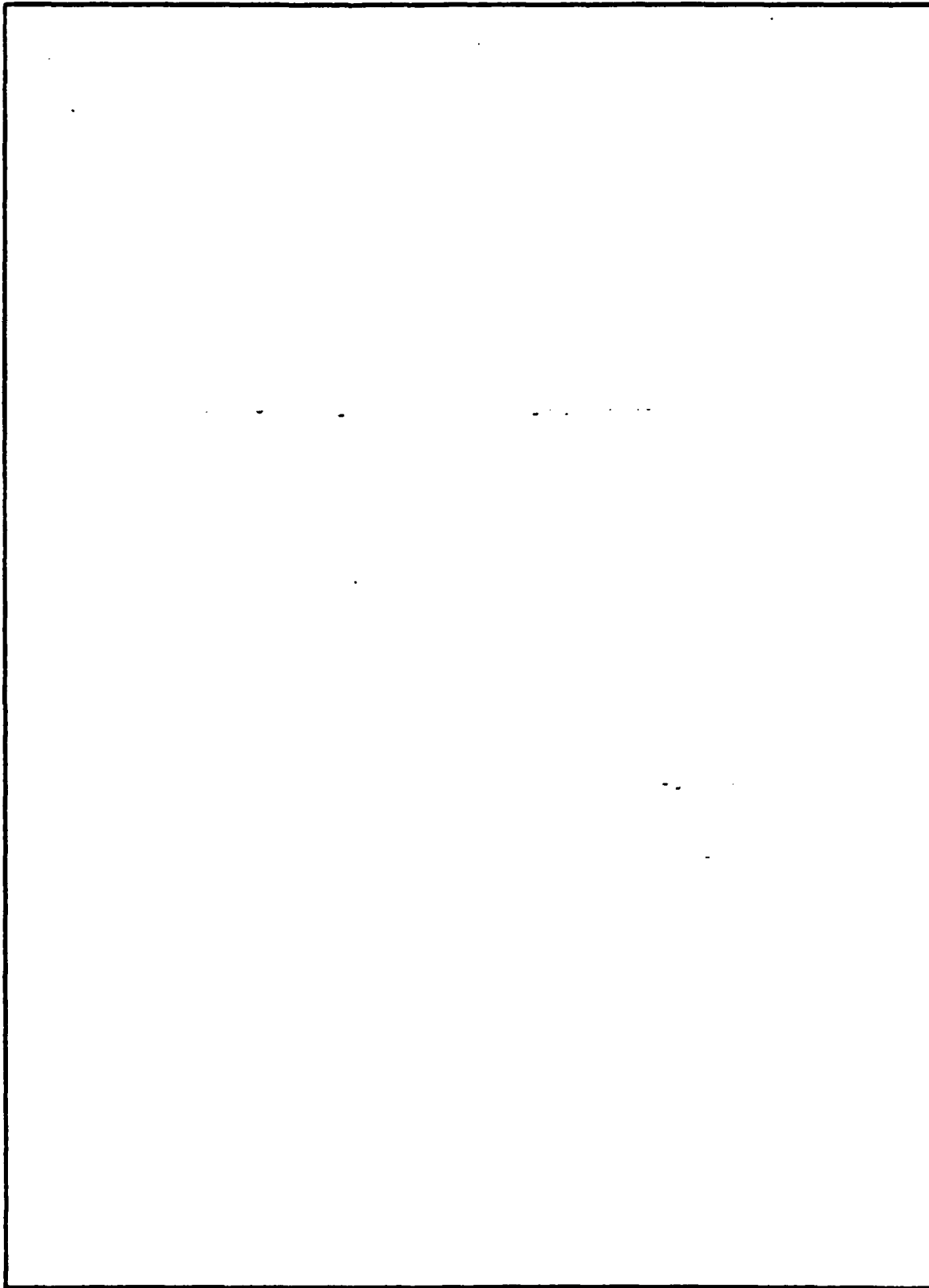
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TECHNICAL REPORT NO. 8

ELECTRONIC STRUCTURE, CHEMICAL BONDING, AND ELECTRON CONDUCTIVITY  
 OF THIN-FILM TRANSITION-METAL SILICIDES

by

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September 10, 1984

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**ELECTRONIC STRUCTURE, CHEMICAL BONDING, AND ELECTRON CONDUCTIVITY  
OF THIN-FILM TRANSITION-METAL SILICIDES\***

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**Abstract**

The local electronic densities of states and chemical bonding of thin-film palladium and molybdenum silicides are compared on the basis of embedded cluster molecular-orbital calculations. Composite Pd(d)-Si(p)antibonding/Si(p)-Si(p)bonding character and composite Mo(d)-Si(p)nonbonding/Mo(d)-Si(d)bonding character at the respective Fermi energies are responsible for the different electrical conductivities of these silicide films and for the different Schottky barriers of the corresponding silicide/silicon systems.

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\*Research sponsored by the Office of Naval Research.

Thin-film transition-metal silicides are being used to an increasing extent as interconnect and gate materials in very-large-scale-integrated (VLSI) circuits [1-3]. Experimental [4-6] and theoretical [7-9] studies, focussed primarily on the near-noble Pd, Ni, and Pt/silicon interfaces and silicides, have established the importance of chemical intermixing and bond formation in determining Schottky barrier height and electron transport across transition-metal silicide/silicon interfaces. Such issues are also expected to be of significance in refractory transition-metal (e.g. Mo, W, and Nb) silicide/silicon interfaces, which are of great current technological interest for high-speed VLSI computer circuits [10], but have not been the subjects of much fundamental experimental or theoretical investigation [11].

In this communication, we present quantitative theoretical models for the electronic structures and chemical bonding of thin-film palladium and molybdenum silicides. Because of the importance of local chemical bonding, the electronic structures have been calculated by a "real-space" molecular-orbital approach rather than a "reciprocal-" or "k-space" band-structure method. The approach used is the recently developed iterative partitioned scattered-wave method [12], which permits the computation of molecular orbitals and local densities of states for subclusters of an extended solid or interface, including the effects of "embedding" the subclusters in the extended environment. This method is combined with the  $X\alpha$  approximation to electron-electron exchange and correlation [13], which has traditionally been used with the scattered-wave method in its conventional form [14,15]. The standard  $X\alpha$  scattered-wave

molecular-orbital method has already been applied successfully to elucidate the local electronic structures of hydrogenated amorphous silicon [16] and crystalline silicon containing substitutional [17,18] and interstitial [19] transition-metal impurities.

In the iterative partitioning version of the scattered-wave technique [12], the secular equation for the molecular orbitals of large silicide aggregates, such as the  $\text{Pd}_2\text{Si}$  monolayer thin films shown in Fig. 1(a) and (b), consisting of the respective encircled  $\text{SiPd}_3$  and  $\text{Pd}_3\text{Si}_6$  subclusters and the surrounding extended silicide environment, can be written in the matrix form:

$$\begin{bmatrix} T_a^{-1} & G_{ab} \\ G_{ba} & T_b^{-1} \end{bmatrix} \begin{bmatrix} A_a \\ A_b \end{bmatrix} = 0 \quad (1)$$

Here  $T_a$  represents the electron-wave scattering matrix of the silicide subcluster and  $T_b$  represents the scattering matrix of the surrounding environment;  $G_{ab}$  and  $G_{ba}$  are matrices which represent the "propagation" of electron waves between the silicide subcluster and its environment; and  $A_a$  and  $A_b$  are the electron wavefunction amplitudes emanating from the silicide subcluster and environment, respectively. To make the solution of Eq. (1) practical, we first contract the matrix of (1) using a simple property of linear algebra [20]. This leads to the matrix equation:

$$(T_a^{-1} - G_{ab} T_b G_{ba}) A_a = 0 \quad (2)$$

for the molecular orbitals of the silicide subcluster, including the effects of coupling to the silicide environment through the terms  $G_{ab}T_bG_{ba}$ . Solving the contracted secular equation (2) is much more computationally efficient than solving the complete secular equation (1). The following iterative procedure is used to solve Eq. (2): First, an energy eigenvalue  $E_0$  is found from the subcluster submatrix  $T_a^{-1}$ , including only the molecular potential field of the surrounding silicide environment. Then the matrix elements of  $G_{ab}T_bG_{ba}$  are calculated using  $E_0$  as the trial energy. Finally, determinants of the matrix

$$[T_a(E)]^{-1} - G_{ab}(E_0)T_b(E_0)G_{ba}(E_0) \quad (3)$$

are calculated at various values of the energy  $E$  until a zero is found. This value of  $E$  (call it  $E_1$ ) is assumed to be an approximate solution of (2). If  $E_1$  differs considerably from  $E_0$ , the procedure is repeated from the second step using

$$E = cE_0 + (1 - c)E_1 \quad (0 < c < 1) \quad (4)$$

as the next energy. In the last step of this procedure, the matrix elements of  $G_{ab}$ ,  $T_b$ , and  $G_{ba}$  are unchanged, so they must be calculated only once per iteration. Therefore, this procedure leads to a very substantial improvement in computational efficiency over the direct solution of Eq. (1).

The resulting local electronic densities of states for the encircled subclusters of the  $Pd_2Si$  monolayers of Fig. 1(a) and (b),

respectively, including the effects of "embedding" the subclusters in the surrounding silicide environment, are shown as the solid and dashed curves, respectively in Fig. 2(a) and (b). Consistent with recent band-structure studies of epitaxial  $\text{Pd}_2\text{Si}$  layers on a Si(111) surface [9], for each monolayer there is a large peak in the density of states between 1 and 3 eV below the Fermi energy  $E_F$ . The peak for layer (b) of Fig. 1 occurs at somewhat lower (more negative) energy, relative to the Fermi energy, and is somewhat broader than the peak for layer (a) of Fig. 1. This is due to the bonding interaction among the the Pd(d) orbitals (i. e. "d-band" formation) of the triangular  $\text{Pd}_3$  clusters in layer (b). The calculated molecular orbitals corresponding to these peaks are Pd(d) nonbonding with respect to the Si(p) orbitals. The secondary peaks immediately below and above the nonbonding peaks correspond, respectively, to Pd(d)-Si(p) bonding and antibonding molecular orbitals. Indeed, the Fermi level coincides with Pd(d)-Si(p) antibonding states. Within layer (a) of Fig 1, these antibonding states are represented by the  $\text{SiPd}_3$  subcluster molecular-orbital wavefunction contour map shown in Fig. 3(a). Within layer (b) of Fig. 1, these Pd(d)-Si(p) antibonding states are actually bonding between the Si(p) orbitals; as revealed by the molecular-orbital contour map shown in Fig 3(b). In other words, for a thin  $\text{Pd}_2\text{Si}$  film consisting of composite layers (a) and (b) of the type shown in Fig. 1, the Fermi level is "pinned" by electronic states of composite Pd(d)-Si(p)antibonding/Si(p)-Si(p)bonding character. These states lie near the top of the Si(p)-Si(p) bonding valence band of silicon and are responsible for the relatively large Schottky barrier

observed for the  $\text{Pd}_2\text{Si}/\text{Si}$  system [11]. As will be demonstrated below, this composite  $\text{Pd}(d)\text{-Si}(p)$  antibonding/ $\text{Si}(p)\text{-Si}(p)$  bonding character at the Fermi energy also largely determines the electrical conductivity of a  $\text{Pd}_2\text{Si}$  thin film.

The calculated local density of states for an  $\text{SiMo}_3$  subcluster of an  $\text{MoSi}_2$  monolayer is shown in Fig. 4. In contrast to the above results for  $\text{Pd}_2\text{Si}$ , the Fermi energy coincides with a high density of  $\text{Mo}(d)$  states which are nonbonding with respect to the  $\text{Si}(p)$  orbitals. These states lie well above the  $\text{Si}(p)\text{-Si}(p)$  bonding states that correspond to the top of the valence band of silicon. They are responsible for pinning the Fermi level and for the smaller Schottky barrier of the  $\text{MoSi}_2/\text{Si}$  system relative to that of the  $\text{Pd}_2\text{Si}/\text{Si}$  system [11]. A close examination of the molecular-orbital topology of these states, as exemplified by the wavefunction contour maps in Fig. 5, reveals that the  $\text{Mo}(d)$  orbitals, while nonbonding with respect to the  $\text{Si}(p)$  valence orbitals, are actually weakly bonding with respect to the virtual  $\text{Si}(d)$  orbitals. Although one usually ignores  $\text{Si}(d)$  orbitals as being relevant to solid-state electronic structure-properties relations, in this situation these orbitals act as a "pathway" for promoting overlap and metallic bonding among the  $d$  orbitals of the  $\text{Mo}$  atoms which are only second-nearest neighbors in the silicide monolayer. It is also evident from these results (see below) that spatially delocalized  $\text{Mo}(d)\text{-Si}(d)$  bonding of the type shown in Fig. 5 is largely responsible for the electrical conductivity of an  $\text{MoSi}_2$  thin film.

The computed molecular orbitals can be used as a basis for calculating the electrical conductivities of these thin-film

silicides via Kubo theory [21]. Kubo's formula for the conductivity can be reduced approximately (for "room temperature") to the form [22]

$$\sigma = 2\pi^2 n e^2 d^2 / h \quad (5)$$

where  $d$  is the molecular-orbital bond distance at the Fermi energy and  $n$  is the bond electron density at the Fermi energy. The Si(p)-Si(p) bond distance in Fig. 3(b) is 3.8A, whereas the Mo(d)-Si(d) bond length in Fig. 5 is 2.6 A. The corresponding values of  $n$ , obtained from the computed molecular-orbital components, are  $3 \times 10^{22}$  and  $2 \times 10^{22} \text{ cm}^{-3}$ , respectively. Substitution of these values of  $d$  and  $n$  in Eq. (5) yields conductivities of  $3.3 \times 10^5$  and  $1.0 \times 10^4 \text{ (ohm-cm)}^{-1}$  for the  $\text{Pd}_2\text{Si}$  and  $\text{MoSi}_2$  layers, respectively, which correspond to resistivities of  $30 \times 10^6$  and  $97 \times 10^6 \text{ ohm-cm}$ . These values are in good agreement with experiment [1]. Thus the difference in the chemical bonding at the Fermi energies of  $\text{Pd}_2\text{Si}$  and  $\text{MoSi}_2$  thin films accounts for their respective electrical conductivities.

In conclusion, it has been shown that the detailed composite molecular-orbital topology of the electronic states around the Fermi energy is key to understanding the specific electrical properties of thin-film transition-metal silicides. Such knowledge may possibly be put to use in the development and refinement of silicide/silicon VLSI microstructures.

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## Figure Captions

Fig. 1. Monolayer structures of  $\text{Pd}_2\text{Si}$ . Solid circles represent Pd atoms; open circles represent Si atoms. The principal subclusters defined in the partitioned scattered-wave molecular-orbital calculations are encircled (dashed circles).

Fig. 2. Subcluster local electronic densities of states for  $\text{Pd}_2\text{Si}$  monolayers (a) (solid profile) and (b) (dashed profile) of Fig. 1, as computed by the partitioned scattered-wave method. The principal chemical bonding, nonbonding, and antibonding characters of the component molecular orbitals are indicated.

Fig. 3. (a) Contour map of the Pd(d)-Si(p) antibonding molecular-orbital wavefunction at the Fermi energy for the  $\text{SiPd}_3$  subcluster of Fig. 1(a) monolayer; (b) contour map of the composite Pd(d)-Si(p)antibonding/Si(p)-Si(p)bonding molecular-orbital wavefunction at the Fermi energy for the  $\text{Pd}_3\text{Si}_6$  subcluster of Fig. 1(b) monolayer. The solid and dashed contours represent positive and negative values of the wavefunction, respectively.

Fig. 4. Subcluster local electronic density of states for an  $\text{MoSi}_2$  monolayer, as computed by the partitioned scattered-wave method. The principal bonding, nonbonding, and antibonding characters of the component molecular orbitals are indicated.

Fig. 5. Contour maps of the  $\text{SiMo}_3$  subcluster Mo(d)-Si(d) bonding molecular-orbital wavefunction at the Fermi energy of an  $\text{MoSi}_2$  monolayer, plotted in (a) the monolayer plane and in (b) a plane perpendicular to the monolayer and containing two Mo atoms. Solid and dashed contours represent positive and negative values of the wavefunction, respectively.

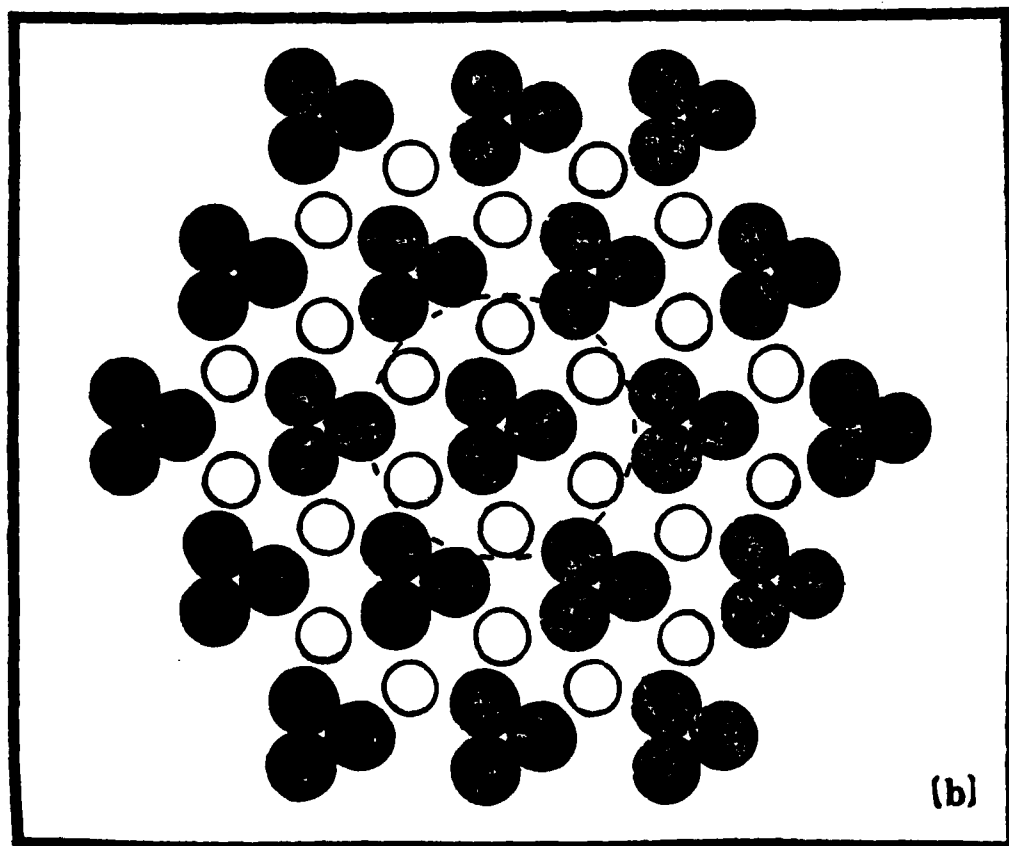
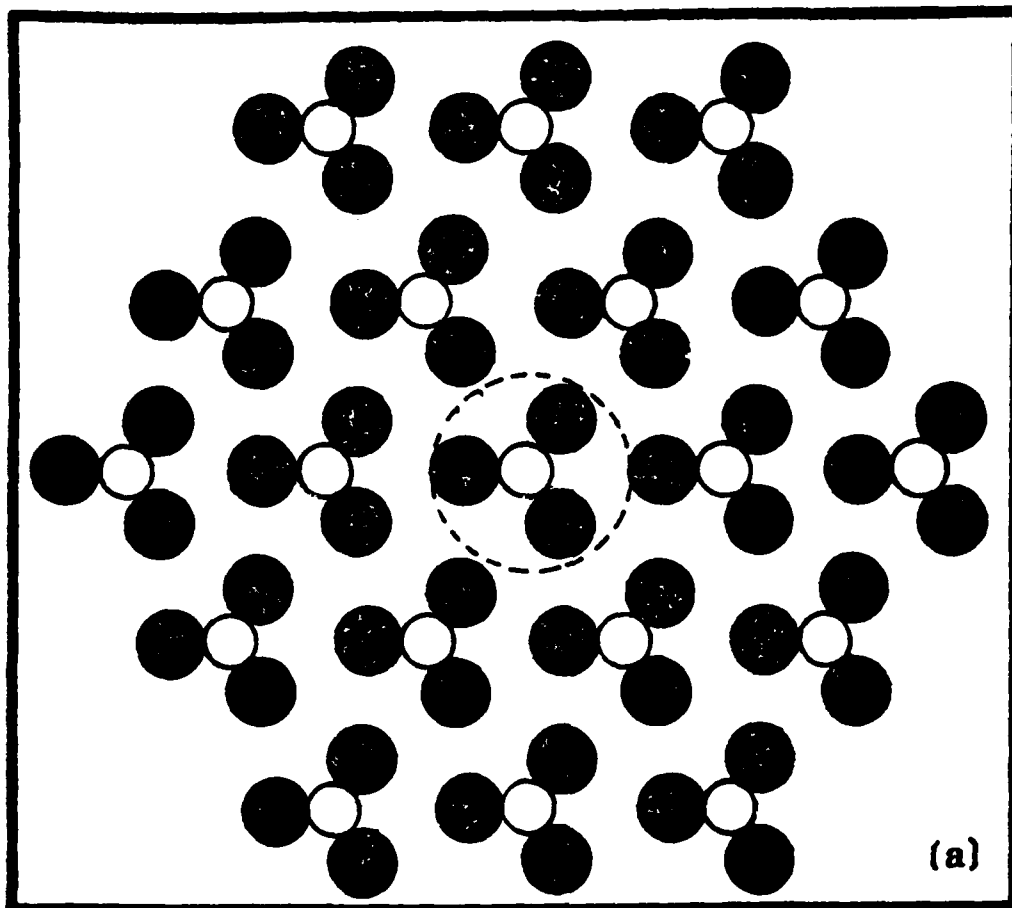


Fig. 1

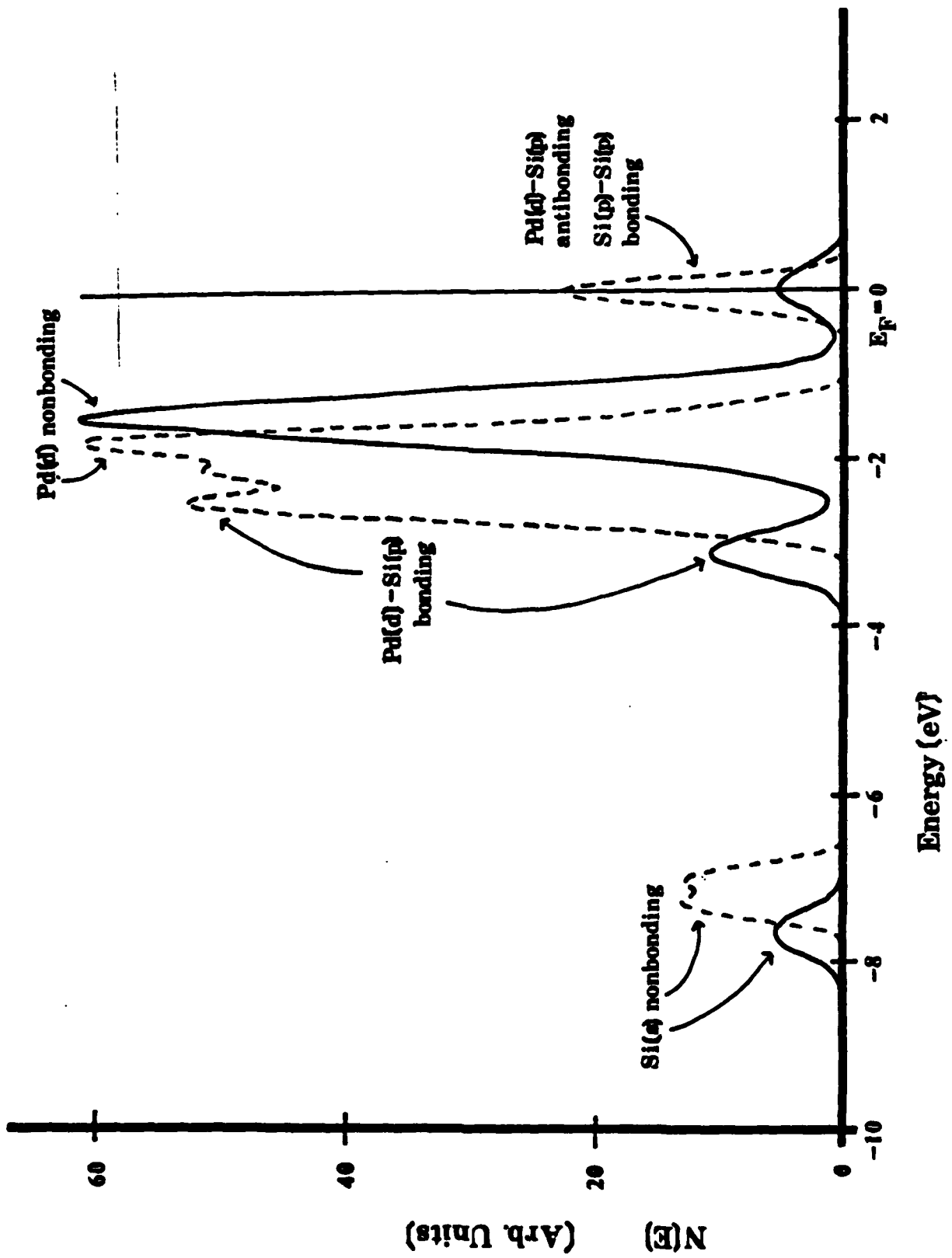


Fig. 2

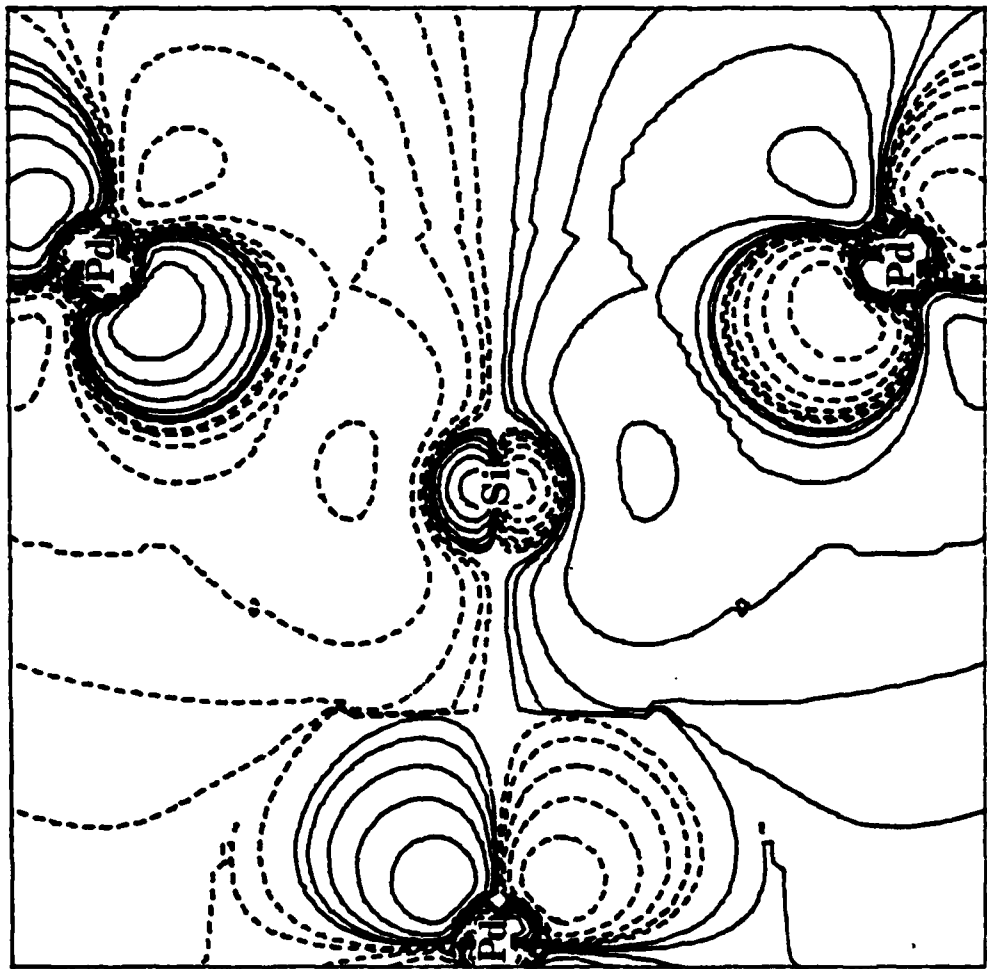


Fig. 3(a)

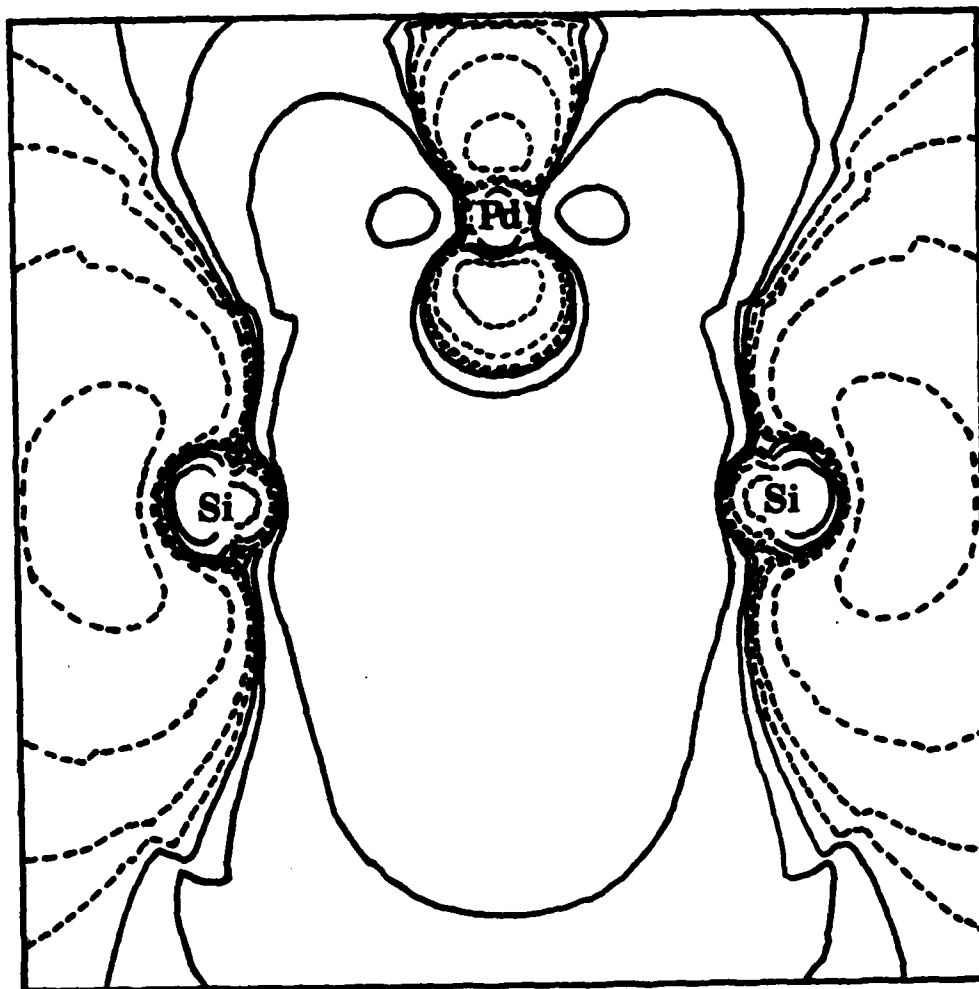


Fig. 3(b)

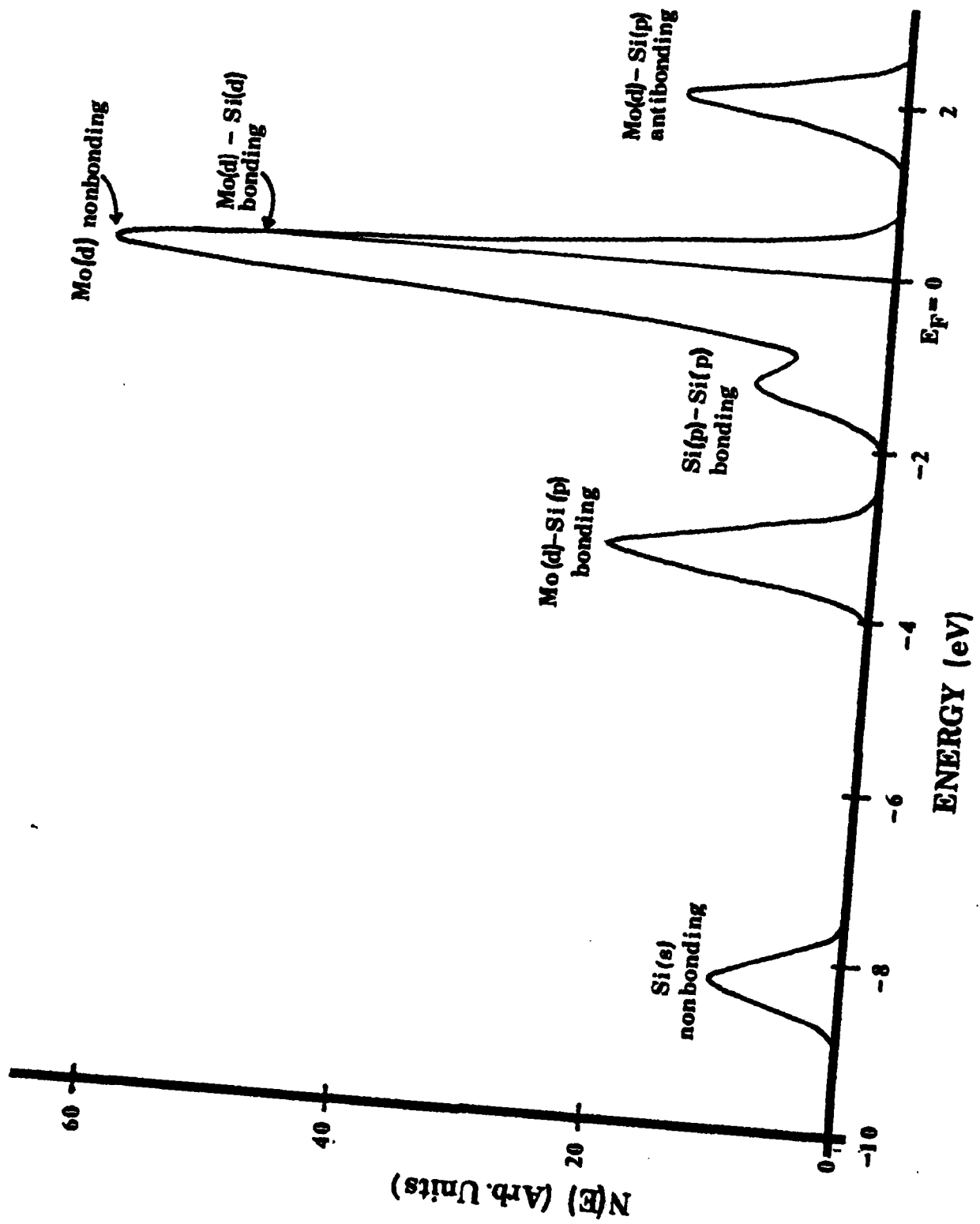


Fig. 4

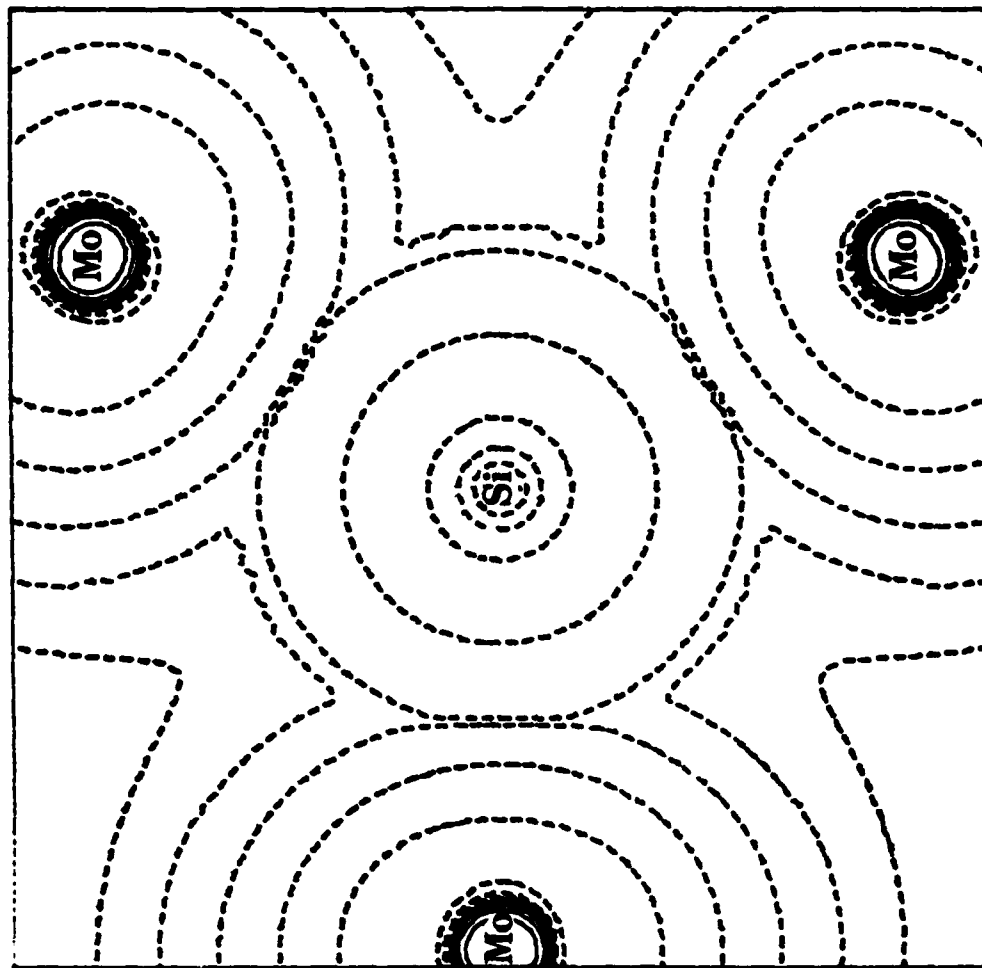


Fig. 5(a)

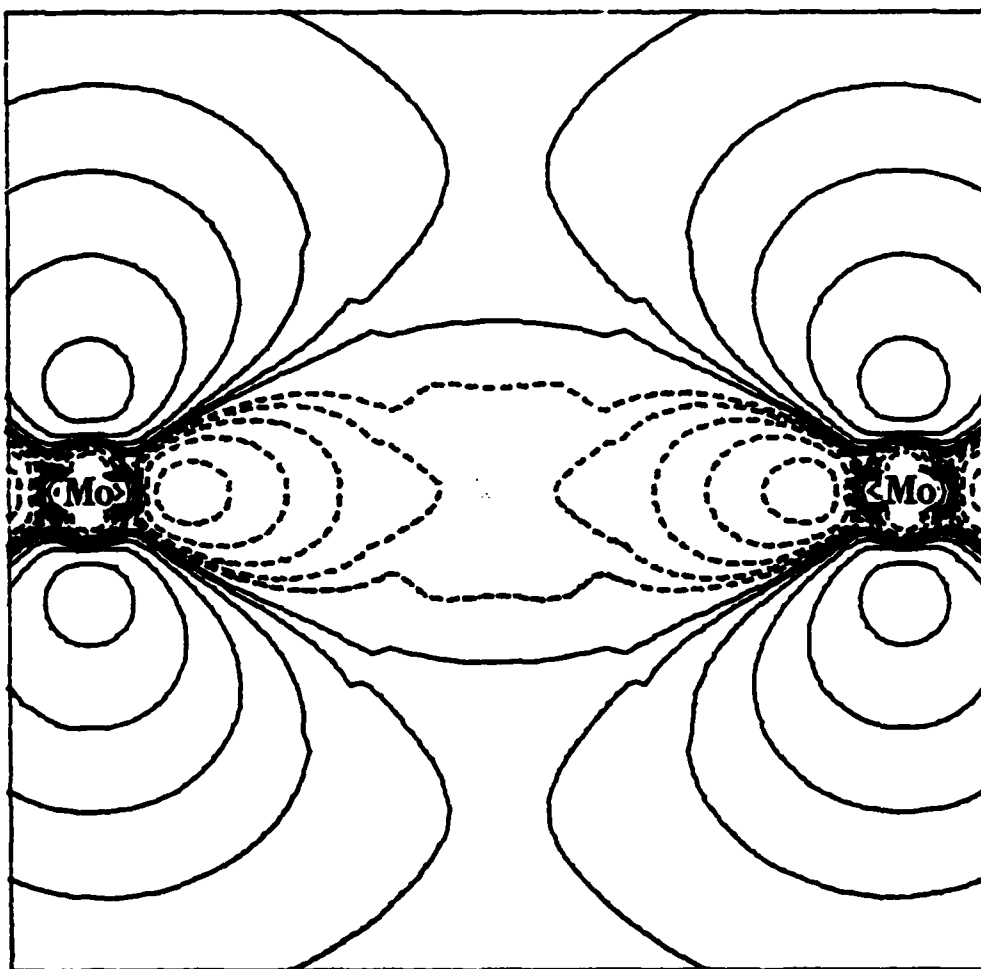


Fig. 5(b)

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