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Magnetic ordering of Ga wires on Si(100) surfaces

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We report on total-energy electronic-structure calculations within the density-functional theory performed for an atomic wire consisting of Ga atoms which are deposited on hydrogenated Si(100) surfaces. We find that there are three distinct stable atomic structures and that the ground state is magnetic in one of the three structures. Stability of the magnetic state against carrier doping and charge-density-wave generation is discussed.

Nanometer scale manipulation of atoms on surfaces has been partly realized by scanning tunneling microscope technique: The controlled deposition of atoms on metal surfaces[1] and on semiconductor surfaces[2] is now relatively facilitated. An important example of such manipulations is the fabrication of a Ga wire on the hydrogenated Si(100) which is a premier surface in semiconductor technology: It has been demonstrated that H atoms on the hydrogenated Si(100) are removed along a Si dimer row,[3,4] and then foreign atoms, Ga atoms in this case, are placed on the H-free array of Si atoms.[4] Microscopically, it is likely that three Ga atoms per two Si dangling bonds are deposited along the array.[4,5] Electronic structure calculations by local-density approximation (LDA) show that there are several metastable geometries for a Ga wire on the hydrogenated Si(100) and that energy bands near the Fermi level (E_F) are extremely flat for some of the geometries.[5] Further investigations using a tight-binding model suggests a possibility of spin polarization along the Ga wire.[6] The wire is then speculated to be an example of flat-band ferromagnetism in which subtle balance of electron transfers among atomic sites induces flat bands and carriers there are spin polarized.[6,7] For definite clarification of magnetic properties of the wire, however, more legitimate first-principles calculations are imperative.

In this paper, we study atomic and electronic structures of the Ga wires on the hydrogenated Si(100) surfaces by the density-functional theory (DFT) with the local-spin-density approximation (LSDA) and the generalized-gradient approximation (GGA) in which spin degrees of freedom are taken into account. Starting from three distinct initial structures which have been reported in the previous LDA calculations,[5] we reach a new stable geometry for each structure. We find that two of the three atomic structures are paramagnetic. However, the remaining structure, which is not substantially different from the other two, is found to be either ferromagnetic or antiferromagnetic. Nearly flat bands along the direction of the Ga wire emerge in the magnetic structure. A detailed analysis of the wave functions reveals that the most of the spin density are distribution around Ga trimers on the Si surface. We thus predict that the Ga wire on Si(100) exhibits the certain magnetic orders with nonmagnetic elements alone.

All calculations have been performed on the basis of the density-functional theory.[8,9] The exchange-correlation interaction is essential to describe magnetism. Hence we use local-spin-density approximation and generalized-gradient approximation and hereby extract common features irrespective of the approximation level. For the exchange-correlation energy, we adopt a functional form by Perdew and Zunger[10,11] in LSDA and by Perdew and Wang[12] in GGA, respectively. Norm-conserving pseudopotentials generated by using the Troullier-Martins scheme are adopted to describe the electron-ion interaction.[13,14] We consider the partial core correction for the Ga atoms in the treatment of the exchange-correlation energy.[15] The valence wave functions are expanded in terms of the plane-wave basis set with the cutoff energy of 10 Ry.[16] The surface is simulated by a repeating slab model in which 8 Si atomic layers and the 5.6-Å vacuum region are included. The bottom of the slab has a bulklike structure with each Si saturated by two H atoms. On the top of the slab, which simulates the real surface, an H adlayer plus Ga atoms are considered. We adopt 4×2 lateral periodicity in which three Ga atoms are included.[4,5] We use the geometries which have been obtained by the previous LDA calculation[5] as initial atomic geometries. Eight k points are used for the integration over surface Brillouin zone. When we examine the stability of the 4×2 structure against the 4×4 modulations such as the charge-density wave or the spin-density wave, a 4×4 lateral cell with five atomic layers is adopted in the calculation. Geometry optimization has been performed for all atoms in the slab except for the bottom-most Si and H atoms. We use the conjugate-gradient minimization scheme both for the electronic structure calculation and for the geometry optimization.[17] In the optimized geometries the remaining forces acting on the atoms are less than 0.005 Ry/Å.

Optimized structures of three stable geometries which are obtained by the GGA are shown in Fig. 1. The LSDA leads to qualitatively same optimized structures. Yet there are sizable differences in structure which cause the modification in energetics, as is shown below. In the three structures, adsorbed Ga atoms form trimers which are aligned in the direction parallel to the Si dimer row. The Ga atoms form covalent bonds with each other and with subsurface Si atoms. Table I shows calculated relative total energies for each structure. The structure A is the most stable among the three structures in the LSDA, whereas the structure B is the most stable in the GGA calculation. The structure C is not a global

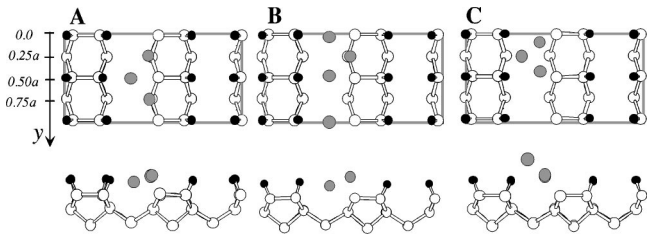

FIG. 1. Top and side views of optimized three atomic structures, A, B, and C, of a Ga wire on the hydrogenated Si(100) surface. White, shaded, and black circles denote Si, Ga, and H atoms, respectively.

minimum in total energy. Yet the total energy of the structure C is higher than that of the most stable structure only by the order of 0.1 eV or less in the GGA. We have also explored atomic reaction pathways from the structure C to the structure B and the corresponding energy barriers in the GGA. The exploration has been achieved by the constrained energy minimization on several N-1 dimensional planes (N is the ionic degrees of freedom).[18] It is found that there is an energy barrier of 0.4 eV along the reaction from C to B. Therefore, the structure C is certainly metastable and realized at room temperature. It is of interest that the calculated relative total energies are considerably different between the LSDA and the GGA. This is partly due to the difference in the obtained structures themselves.[19]

In the structures A and B, electron spin is not polarized: We only find paramagnetic solutions. In the structure C, however, we find both paramagnetic and ferromagnetic states (we also find an antiferromagnetic state described below). The calculated number of polarized spin in the ferromagnetic state is one per unit cell. The ferromagnetic state is lower in energy than the paramagnetic state by 0.15 (0.07) eV in the GGA (LSDA) (Table I). As a result, the ferromagnetic state in the structure C is higher in energy only by 28 meV in the GGA than the most stable paramagnetic state in the structure B. A considerable portion of the Ga wires is therefore taking the structure C and spin-polarized in thermodynamic conditions. From these energetics, along with the energy barrier for the structural change stated above, it is likely that the Ga wire on Si(100)/H takes the structure C and becomes a nanometer scale magnet consisting of nonmagnetic elements alone.

The electronic energy bands, which are obtained by the GGA, of the three optimized structures are shown in Fig. 2.

TABLE I. Relative total energies E (eV) per unit cell obtained by LSDA and GGA. The energy is measured from the structure A. In the structure C, both paramagnetic and ferromagnetic spin configurations are obtained, whereas only the paramagnetic configuration is obtained in A and B. The number of polarized electrons, $\Delta = n_{\mathrm{up}} - n_{\mathrm{down}}$, is a difference of the number of up spins (n_{up}) and down spins (n_{down}).

		A	B	C	
				Para	Ferro
E (eV)	LSDA	0	0.279	0.444	0.376
	GGA	0	−0.001	0.173	0.027
Δ	LSDA, GGA	0	0	0	1

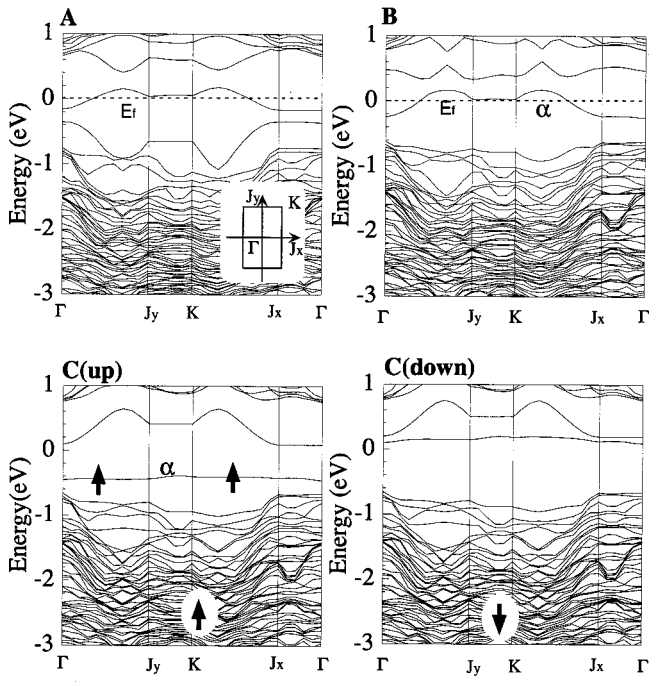

FIG. 2. Energy bands of a Ga wire on Si(100)/H with the atomic structures A, B, and C shown in Fig. 1. In the cases of A and B structures, the energy bands for up and down spins are degenerate. In the structure C, the highest occupied band splits by ~0.6 eV for up and down spins, and the band only for the majority spin is occupied. The directions $\Gamma - J_y$ and $\Gamma - J_x$ are parallel and perpendicular, respectively, to the Ga wire.

Since the structure C has ferromagnetic electronic structure, we show energy bands for both up and down spins. In all structures, the electron state α around E_F exhibits extremely small dispersion along the direction perpendicular to the wire (an isolated Ga wire is generated experimentally, whereas Ga wires are separated by 15.34 Å in the present supercell calculations). This means that the interaction between the adjacent wires is sufficiently small. Along the direction parallel to the wire, the state α shows substantial dispersion (~0.4 eV) in the structures A and B. In the structure C, however, the state α exhibits small dispersion even along the direction parallel to the wire: The flat band with a width of less than 50 meV emerges in the structure C. This feature of the flat band renders the electron states in the structure C spin polarized.

Figure 3(a) shows the spin density in the ferromagnetic state in the structure C. The spin is polarized only in the highest occupied state α. The spin density is primarily distributed on Ga trimers. Yet it penetrates to subsurface Si atoms. The value of the spin density around the Ga trimer is four times larger than those at the subsurface Si atoms and in the inter-Ga-trimer region ($y = 0.75a$ in Fig. 3). This localized nature certainly causes small dispersion of the α band and thus ferromagnetic ground state. Figure 3(b) shows the charge density of the highest occupied band α in the paramagnetic state in the structure B. Again the charge density is primarily around the Ga trimer and penetrates to subsurface Si atoms. Yet when we compare (a) and (b) of Fig. 3 in detail, it is concluded that the charge density of the paramagnetic state in the structure B extends in the inter-Ga-trimer region compared with the spin density in the structure C.

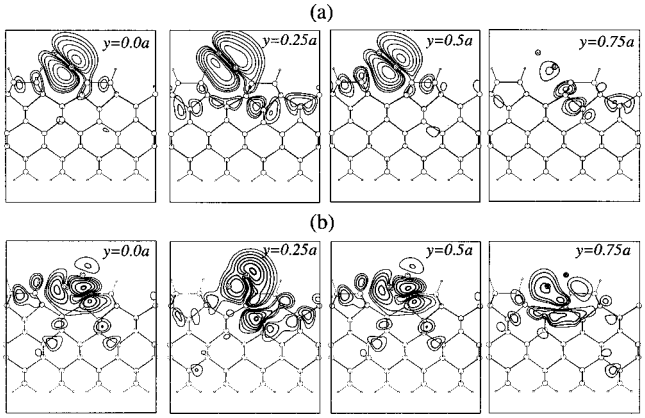

FIG. 3. Contour maps of the squared wave functions of (a) the highest occupied state α (Fig. 2) in the structure C (Fig. 1), and of (b) the partially filled state α at E_F in the structure. B. Each map is drawn on the four distinct phases perpendicular to the surface shown in Fig. 1. White and shaded circles are Si and Ga atoms, respectively. The lowest value represented by the contour is 0.00105 e/Å^3 for (a) and (b). Each contour represents twice (or half) the density of the adjacent contour lines.

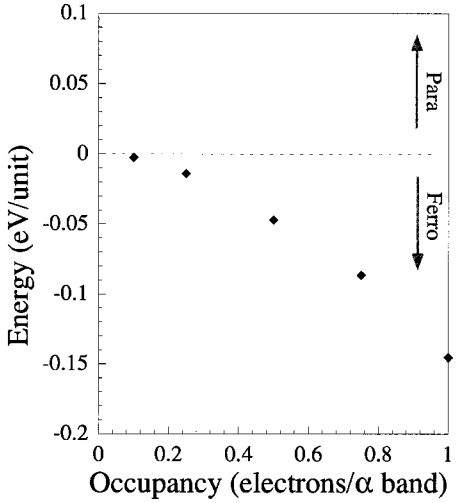

FIG. 4. Total-energy difference $E_{\text{ferro}}-E_{\text{para}}$ between the paramagnetic and the ferromagnetic states as a function of the number of holes n_h doped in the flat band. The structure is fixed to the obtained structure C in Fig. 1.

It is important to examine the stability of the ferromagnetic state in the structure C against temperature, the carrier doping, the charge-density-wave (CDW) generation, and the antiferromagnetic (AF) ordering. It may be inappropriate to evaluate the critical temperature for the ferromagnetic state from the total-energy difference in density-functional theory. Yet the value $E_{\text{ferro}}-E_{\text{para}}=-0.15$ eV in the present GGA calculation is smaller than but comparable with the values obtained in the density-functional theory for typical bulk ferromagnets such as Fe, Co, and Ni.[20] Further the Ga wire is not a pure one-dimensional system: Electron transfers occur via Si atoms below the Ga trimer as well as in the interwire region. It is thus likely that the present Ga wire exhibits the magnetic ordering at sufficiently high temperature.

In Fig. 4, we show the total-energy difference between the ferromagnetic and the paramagnetic states in the structure C as a function of the number of holes doped in the flat band α. It is found that the ferromagnetic state is energetically favorable compared with the paramagnetic state for all numbers of holes. The difference is approaching zero with increasing the hole number, as is expected. The present ferromagnetic state is quite robust against carrier doping.

To assess the possibility of the CDW ordering, we study geometric and electronic structures using the 4×4 lateral supercell with five atomic layers. We start with the structure in which one of the two Ga trimers is shifted along the wire direction by 0.2 Å. It is found that the trimer migrates to the initial position and the structure C is thus recovered. The electronic spin structure is also unchanged. Hence, the obtained ferromagnetic state in the structure C is stable against the lattice distortion with double periodicity.

We then examine the total energy of the AF spin arrangement. We use the 4×4 lateral supercell with five atomic layers. It is found that the calculated total energy is almost identical to that of the ferromagnetic state at the present accuracy. This finding sheds light on the mechanism of appearance of the ferromagnetic state in the present Ga wire. In the flat-band ferromagnetism, the Bloch states in the flat bands are generally extended, and some localized orbitals transformed from the Bloch states overlap each other. Then, when spins accommodated in the localized orbitals are parallel, the cost of the electron-electron repulsive energy is reduced on average compared with the antiparallel configuration. The flat band in the present Ga wire is unlikely to be the case: The distribution of the electron density in the structure C [Fig. 3(a)] is quite localized around the Ga trimer. We thus provisionally conclude that the spin is polarized in the structure C due to the localized nature of the relevant electron state and that the magnetic ordering, i.e., the ferromagnetic or the antiferromagnetic, is determined by weak exchange coupling between the polarized spins. The magnitude of the exchange coupling is small so that the determination of the magnetic ordering is not feasible in the present scheme of the calculation.

In summary, we have studied atomic and electronic structures of Ga wires on the hydrogenated Si(100) surfaces by using the local spin-density approximation and the spin-polarized generalized-gradient approximation. We have obtained the three stable structures. We have found that either the ferromagnetic or the antiferromagnetic ground state is realized in one of the three structures. The other two structures show only the paramagnetic state. In the magnetic state, nearly flat bands near E_F along the direction parallel to the Ga wire has been found. This flat band is due to relatively localized nature of the spin density of Ga trimers. The present results may be the first theoretical indication that a nanometer-scale magnetic ordering is possible on semiconductor surfaces using nonmagnetic elements alone.

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