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PAPER

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Effect of impurities on the growth and morphology of cementite nanowires

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Abstract

The effects of doping on the morphology of iron carbide (cementite) nanowires have been explored by first principles electronic structure calculations. We examined the role of several realistic impurities (Si, Mn, V, P and S) in the formation energies of cementite nanowires with different sizes and morphologies. It is shown that the presence of the impurities decreases the formation energy and can switch the preferable axis of the cementite nanowire growth. The conditions of the formation and decomposition of cementite nanowires in steels are also discussed.

(Some figures may appear in colour only in the online journal)

1. Introduction

Fabrication of nanowires and nanorods with a given morphology is one of the most explored subjects in modern nanoscience [1–21]. Whereas semiconductor [1–7], elemental-metal [8–11] and metal-oxide [12–15] nanowires have been discussed in many works, the formation of metal-carbide nanostructures has only been reported for a few metals (Al, Ti and Mo) [16–19]. Recent experimental works [5–7] for the case of semiconductor nanowires demonstrate that impurities can be catalysts of nanowire formation and determine its morphology. These results show that doping can play a role not only in the conditions of production of nano-objects but also in their morphology and phase transitions. In previous theoretical works the segregation of various impurities near the surface of semiconducting nanowires has been explored [20–25]. The changes in the electronic structure caused by the presence and segregation of impurities were considered. However, neither the influence of impurities on the formation energies nor possible changes in the morphology were discussed. It is important therefore to examine the role of doping for the morphology of realistic nanowires.

Iron carbide (Fe_3C or cementite) nanostructures have been obtained as secondary phases in the processes of

fabrication of iron-filled carbon nanotubes [26, 27]. The detection of cementite nanowires in ancient (12th century AD) sabers [28] made from the famous Damascus steel (DS) [29] raised the question about the necessary conditions for the growth of metal-based nanowires. So, studies of the physical mechanisms of the formation of cementite nanowires have both fundamental interest and importance for the whole nanofabrication area. The experimental results [30–34] give evidence of an important role of impurities for the unusual structure and properties of DS. It requires a detailed survey of the role of realistic impurities in the formation and morphology of the freestanding cementite nanowires.

In our work we study the energetics of pure and doped cementite nanowires grown along three possible directions and discuss the possible ways of decomposition of the cementite nanowires with formation of different carbon-based nanostructures [35, 36]. We show that different impurities result in the growth of the cementite nanowires along different axes.

2. Computational method and model

The modeling is carried out using the density functional theory (DFT) implemented in the pseudo-potential SIESTA

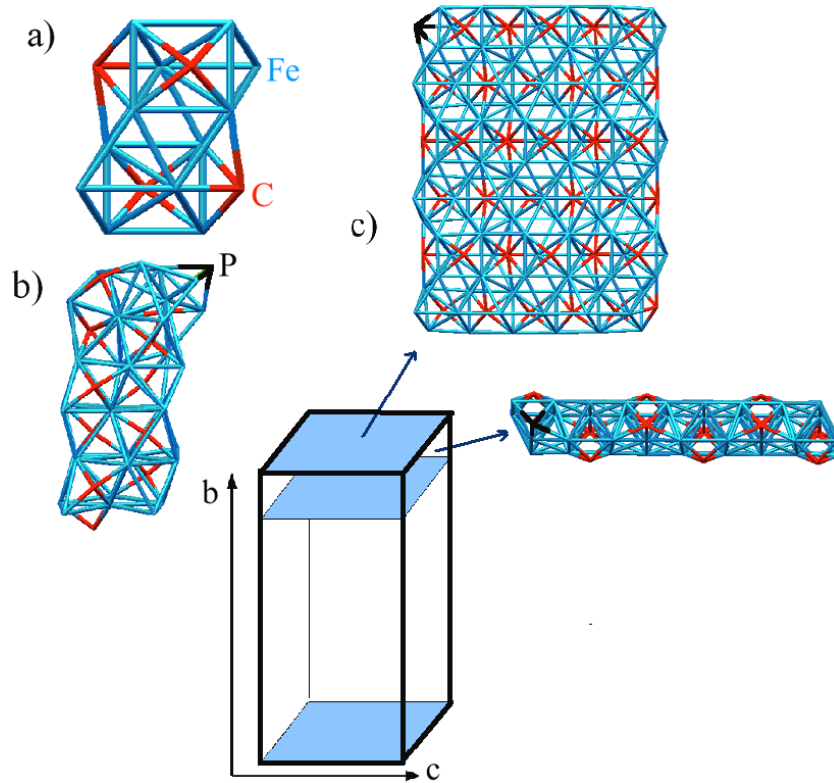


Figure 1. Optimized crystal structure for the cementite unit cell (a); supercell of cementite nanowire with the minimal width ($1a \times 3b \times 1c$) doped by P (b); side and top view of the supercell with the minimal length and with width 4.44 nm ($3a \times 1b \times 3c$) also doped by P (c). Iron atoms are shown by blue, carbon by red and phosphorus by black.

code [37]. All calculations are done in the generalized gradient approximation (GGA) [38] with spin polarization. Full optimization of the atomic positions was performed. During the optimization, the ion cores are described by norm-conserving non-relativistic pseudo-potentials [39] with cut-off radii of about 2.25 au for 3d elements and about 1.25 au for light elements used in calculations, and the wavefunctions are expanded with a double- ζ plus polarization basis of localized orbitals for carbon and oxygen, and a double- ζ basis for hydrogen. Optimization of the force and total energy was performed with an accuracy of $0.04 \text{ eV } \text{\AA}^{-1}$ and 1 meV, respectively. All calculations were carried out with an energy mesh cut-off of 360 Ryd and a k -point mesh of $4 \times 4 \times 4$ in the Monkhorst–Park scheme [40]. These technical parameters are chosen to be similar to those in our previous work on iron-carbon systems [41]. We define the formation energy of the cementite nanowires as $E_{\text{form}} = E_{\text{nanowire}} - E_{\text{bulk}}$, where E_{bulk} is the total energy of a cementite supercell in the bulk in the same magnetic configuration. For the case of cementite with impurities, E_{bulk} is the total energy for the supercell of cementite with the same concentration and disposition of impurities as in the nanowires. For the simulation of nanowires we use a cementite supercell (see figure 1) within the periodical boundary conditions along selected crystallographic axes and separated by 5 nm of empty space between nanowires.

3. Results and discussions

In the present work we consider the effect of different impurities on the morphology of cementite nanowires. We have performed our modeling for both pure and doped nanowires oriented along different crystallographic axes. Mn and Si were chosen as the most common impurities (of course, apart from carbon) in ordinary steels, V is also used in the high-strength low-alloy steels [29] and P, S and V were experimentally found in DS [27, 28, 34]. The calculations were performed first for the ferromagnetic ground state of cementite. However, the morphology of cementite in steels at high enough temperature (in particular, above the Curie temperature) is also of great interest. To study the effects of changes in magnetic state induced by the temperature, we have also performed calculations for disordered magnetic configurations [42, 43]. More specifically, calculations for three different randomly chosen spin configurations with the total magnetic moments equal to zero, which models the high-temperature paramagnetic state, have been performed for the bulk cementite and the nanowires. During the optimization of atomic structure we keep the chosen magnetic configuration. In all studied disordered configurations we have found a decrease of formation energies of cementite nanowires. For the smallest (1.24 nm) width of the nanowire oriented along the c axis it changes from 5.10 to 4.95 eV/Fe₃C for the pure case, from 4.95 to 4.70 eV/Fe₃C for P-doped

and from 5.21 to 5.13 eV/Fe₃C for Mn-doped cases, in comparison with the ferromagnetic states. Thus, the degree of magnetic order of cementite plays an insignificant role in the energetics of the formation of pure and doped cementite nanowires.

In contrast to elemental iron, the crystal structure of cementite is strictly anisotropic and can be described as a layered system with alternation of two iron and one carbon layers perpendicular to the crystallographic *b* axis (see figure 1). The axes in the cementite are chosen according to the standard denomination of the axes in the cementite lattice used in the previous works [28]. This special crystal structure determines the anisotropy of lattice distortions in the presence of impurities. Our calculations demonstrate that all impurities (Mn, V, Si, P, S) studied in this work produce an expansion of cementite along the *a* and *c* axes and an insignificant compression along the *b* axis. Substitution of a iron atom by silicon or manganese provides a smaller lattice expansion than the substitution of a carbon atom by phosphorus or sulfur (0.5 and 2% for Mn and S, respectively). This tendency in cementite lattice expansion is due to a big difference between carbon and phosphorus ionic radii (0.15 versus 0.37 Å); the difference between iron and manganese ionic radii is much smaller (both are about 0.6 Å). The insignificant changes of structural anisotropy for bulk cementite discussed above can be more important in the nanophases.

Further modeling requires a specification of the model for the chemical composition of cementite nanowires. First of all, we studied the disposition of impurities inside the nanowires. We calculated the total energies of cementite nanowires of width 4.44 nm with Mn or P impurities situated at different distances from the center of the wire. For both types of impurities the substitution of the surface host atom by the impurity atom (see figures 1(b) and (c)) turned out to be more favorable than the substitution of the host atom in the center of the nanowire. For manganese and phosphorus this difference is 0.48 eV/atom and 0.72 eV/atom, respectively. The calculated energy difference between these two types of impurities is caused by the deeper relaxation near the surface of nanowires in contrast to the bulk region. This result is similar to the previously obtained computational results for the impurity segregation in semiconductor nanowires [20–25].

The second step of the model definition is the evaluation of the length and the width of the supercell used for the calculations of doped cementite nanowires. We examined the role of width and length for manganese and phosphorous as typical impurities for the substitution of iron (Mn) and carbon (P) in cementite. For computational simplicity we used for this check the cementite nanowire of the minimal width only (0.6 nm), as shown in figure 1(b). We increased the length of the supercell, which corresponds to the increase in the distance between the impurities along the nanowire. The computational results (figure 2(a)) suggest that the distances between impurities along the nanowire are insignificant. For the case of impurities separated by distances of more than 1 nm the effect is really small, due to a decay of the lattice distortions. In contrast to the length of nanowires, the increase of their widths provides an exponential decrease of

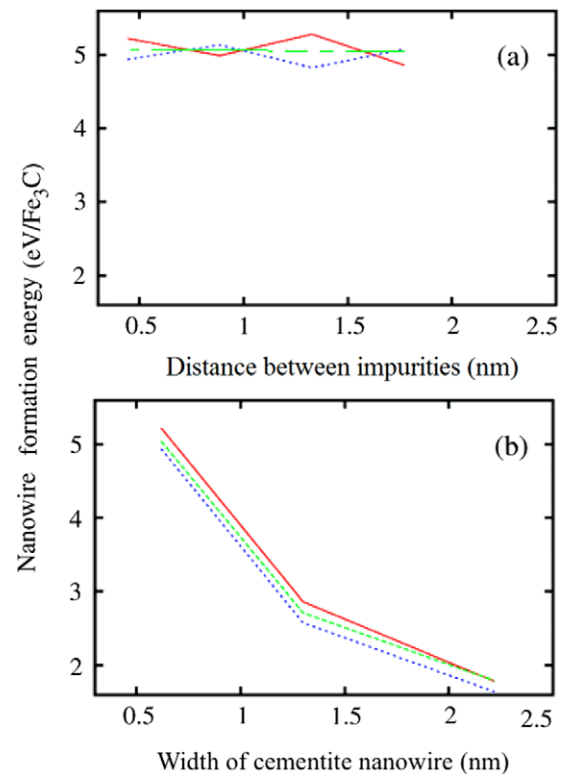


Figure 2. Formation energy of pure (dashed green line), Mn-doped (solid red line) and P-doped (dotted blue line) cementite nanowires as a function of the distance between impurities in nanowires of minimal width (a) and nanowire width for the supercell of minimal length (b).

the formation energy for pure and doped cementite nanowires (figure 2(b)). At further increase of the nanowire width the properties of nanosystems approach those of the bulk, the formation energies decreasing. This situation is opposite to increasing the distance between impurities along nanowires because in that case relatively weak bonds between layers make the properties of a supercell with minimal length approximately the same as the properties of bulk cementite. Further calculations of the dependence of formation energies on the width of the cementite nanowires (see figure 3) demonstrate similar tendencies for the decrease of formation energies with the increase of the radii of the cementite nanowires for both types of impurities (V, Mn, Si as substitutes of iron versus P, S as substitutes of carbon).

Next, we consider the results for nanowires of different width (1.24, 2.60 and 4.44 nm) with the minimal length of the supercell. The smallest value corresponds to the minimal width of the cementite unit cell and the bigger one is close to the experimentally observed thickness of these nanowires [22]. First of all, it is worthwhile noting that, independently of the type of impurities and the width of nanowires, the formation energy for the nanowires grown along the *a* axis is higher than that for other directions, the difference is about 0.4 eV per Fe₃C unit. Further we will discuss only the results for the nanowires oriented along the *b* and *c* axes. The computational results are presented in figure 3. One can conclude from the obtained data that

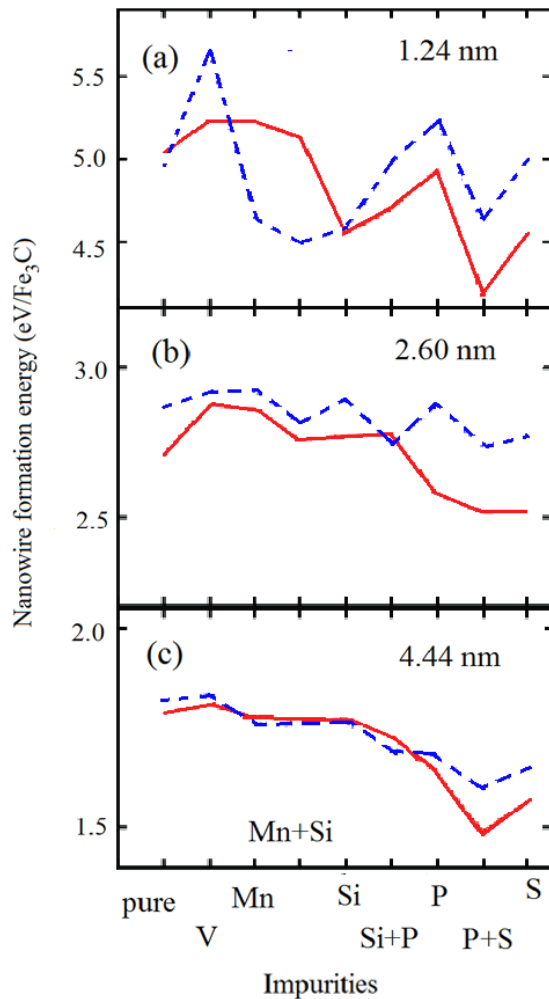


Figure 3. Formation energy of cementite nanowires dependent on the type of impurities for different nanowire morphology (growing along the c axis—solid red line, along the b axis—dotted blue line) for the case of different widths.

vanadium plays no role in the morphology of cementite nanowires. Manganese and silicon strongly suppress the formation of cementite nanowires oriented along the b axis. For pure cementite nanowires with a larger width the tendency of growth along the same axis was also observed. The presence of Mn and Si impurities only decreases the formation energy of nanowires, due to a decrease of the corresponding surface energy.

For the cases of phosphorus and sulfur, the aforementioned reduction of the formation energy has been obtained. However, it is worthwhile noting that the reduction of the formation energy for P and S doping is stronger than for Mn and Si and for the nanowires of realistic sizes this decrease is about 1/6 and the resulting formation energy of the doped nanowire is less than 1.5 eV (figure 3(c)). We have also examined the role of a combination of similar (Mn + Si and P + S) and different (P + Si) impurities and found that the combination of manganese or phosphorous with silicon impurities does not change significantly formation energies of the cementite nanowires in contrast to the combination of phosphorous and sulfur which significantly decreases the

formation energy for the case of the nanowire grown along the c axis. More significant changes of the structural anisotropy of the bulk cementite provide a switch of the preferable axis from b to c .

Since the magnetic order does not have a qualitative effect on the energetics of nanowires, as was discussed above, these results seem to be feasible for temperatures above the Curie temperature as well. As a result, the changes in the morphology of doped cementite nanowires considered here should take place also for the realistic conditions of metallurgical processes. Ancient DS samples contain an enormous amount of phosphorous and sulfur and a rather low amount of manganese and silicon. Interestingly, the cementite nanowires oriented along the c axis were found in P- and S-rich samples of DS [31, 34]. Our results explain this observation.

For temperatures above 750 °C, the decomposition of bulk cementite into α -iron and Kish graphite is observed. This process can be described as a removal of iron layers from the spaces between carbon layers in bulk cementite keeping the layered structure of carbon that leads to the formation of graphite and iron [44]. In the case of decomposition of the cementite nanowires, different carbon nanostructures could appear. For the nanowires oriented along the b axis with carbon layers perpendicular to the main axis, the formation of nano-graphites can be realized. This case is similar to the ordinary decomposition of bulk cementite with Kish graphite formation. In the opposite case (nanowires grown along the c axis) multilayer graphene nanoribbons a few nanometers wide can probably be obtained. We can speculate that, according to the recent experiments for multiwall carbon nanotubes unzipping to graphene nanoribbons [45, 46], a reverse process can be realized at high temperatures and oxygen-free conditions as was discussed in [47]. This process may cause the intriguing appearance of multiwall carbon nanotubes in the ancient DS sabers [36] which can be formed from experimentally observed cementite nanowires oriented along the c axis [28]. Thus, we can conclude that the presence of impurities can play a role not only for the formation and morphology of nano-objects but, in the case of cementite nanowires, it could be important for the formation of other nanostructures appearing after cementite decomposition by annealing in the metallurgical processes.

4. Conclusions

In summary, we can conclude that the performed DFT modeling demonstrates an important role of impurities in the growth and morphology of the cementite nanowires. All impurities considered here decrease the formation energy of cementite nanowires and make cementite nanowires more robust in a realistic environment. Manganese and silicon impurities, common in usual steels, cause the growth of these nanowires along the b axis. In contrast, the presence of phosphorus and sulfur leads to the most significant decrease of the formation energy of cementite nanowires and their growth along the c axis. These results may be relevant to explain the formation of cementite nanowires oriented along the c

axis in ancient samples of Damascus steel, which is usually phosphorous and sulfur rich. The switch of the growth axis of cementite nanowires by the different dopants found in our modeling corresponds to the different structural distortions of the bulk cementite by the same impurities. Doping as a source of enhancement or suppression of anisotropy of host materials can play an important role for the design of novel nanomaterials.

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