Effects of terminated atoms, porosity and drilling orientations on the band structure of porous silicon

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ABSTRACT

We designed different models of nano porous silicon terminated by hydrogen or oxygen atoms, and analyzed their band gap structure and density of states by means of first-principles density functional theory calculation. For the hydrogen-atom-passivation porous silicon in the [1 0 0] direction, with the increase of porosity, the band gap increased. When the porosity is 64%, a direct band gap is obtained. The theoretical results were confirmed by our experiments. For the oxygen-atom-passivation porous silicon in the [1 0 0] direction, half-metallic behavior and ferromagnetism appear when the porosity is 64%, which is due to the Si 3p band affected by O 2p and H 1s orbitals. For the oxygen-atom-passivation porous silicon in the [1 1 0] direction, a direct band gap occurs when the porosity is 49%. Passivation atom, porosity and hollowed-out direction are key factors affecting the band gap structure and density of states of porous silicon. These results would have significant impacts on design of complex porous silicon structures for silicon band-gap engineering in the area of optoelectronics.

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1. Introduction

Silicon is the most dominant material used for microelectronic devices in world semiconductor industry. But its indirect band gap restricts its applications in electro-optical fields. Compared to bulk material, porous silicon (PS) led to a dramatic change of properties due to quantum confinement effects [1,2]. Porous silicon, discovered by Uhlir in 1956 [3], is a form with nanopores in its microstructure. In 1990, Canham [4] observed the photoluminescence of porous silicon at room temperature, which attracted the attention of researchers [5]. However, the luminescence efficiency of porous Si has been low due to its indirect band gap. Surface passivation plays a crucial role in adjusting the properties of porous silicon [6–9]. Experimentally, the luminescence intensity of the porous silicon passivated by H, O, N atoms were increased by several times [6]. The Si dangling bonds on the nanopore surfaces were terminated with these passivation atoms to eliminate midgap defect states which contribute to nonradiative recombination. Theoretically, passivation of dangling bonds with hydrogen atoms leads to substantial transformation of electronic energy structure of Si nanostructure [8,10]. At complete passivation of the dangling silicon bonds by hydrogen atoms, the band gap value

substantially exceeds that for bulk silicon. The incomplete passivation makes the band gap value decrease down the semimetallic range [8]. The oxygen-terminated silicon nanonets (SiNN) were calculated and the oxygen functional groups are found to effectively preserve the direct band-gap nature of the SiNN. The modification of the band properties can be traced to the interaction between the Si 3p and O/N 2p-states, which effectively change the state compositions near the band edge [11,12]. Porosity is another important factor in tuning the properties of PS [13]. The band gaps tend to be quasi-direct for large pore spacing [14]. This is explained by the multiple folding of the Brillion zone along the quantum-confined direction.

In this work, we employed two different functional groups (—H, and —O—) to terminate the dangling bonds of the PS with different porosity and orientation, and analyzed the energy band structure and density of states. For the porous silicon with hydrogen passivation in the [1 0 0] direction, the direct band gap appears with the increase of the porosity. For O passivation model, when the porosity increases to 64%, the conduction band passes through the Fermi level, which shows us a possible method to make half-metallic PS through manipulating the surface passivation [15]. The ferromagnetism was also observed in this model. For the [1 1 0] orientation, we obtained a direct band gap for the O-passivated porous Si.

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2. Models of porous silicon, computational and experimental details

The [1 0 0] and [1 1 0] nanoporous Si were investigated in this work. [1 0 0] and [1 1 0] indicates the drilling directions. The dangling bonds on the nanopore walls are terminated by different atoms. We choose H and O atoms to passivate the PS. Fig. 1(a, b) are the [1 0 0] and [1 1 0] porous silicon structure without passivation atoms, respectively. The special high-symmetry points and axes in the first Brillouin zone (FBZ) of these nanostructures are shown in Fig. 1(c). For the [1 0 0] nanoporous Si, most of the silicon atoms on the pore walls have two dangling bonds except for the corners (Fig. 1(d, e)). For the [1 1 0] structure, there is only one dan-

gling bond for each silicon atom on the pore wall. When oxygen atom is used for passivation, the Si atoms in the corners are passivated by H in order to reduce the internal stress (Fig. 1(f, g)). The coordinate axes in the reciprocal space are established corresponding to the axes of the real space, shown in Fig. 1(d–g). In Fig. 1, Pn means the porosity of the nanoporous silicon. TH means the nanowalls terminated by H, while TO indicates the nanowalls terminated by O. we use these labels in the following text. The nanostructures were fully relaxed by a first-principles total energy calculation using ultrasoft pseudopotential (USPP) [16]. All first-principles calculations in this study have been performed with the CASTEP codes [17]. The calculations of the energy band structure of the silicon nanonets were based on the local density
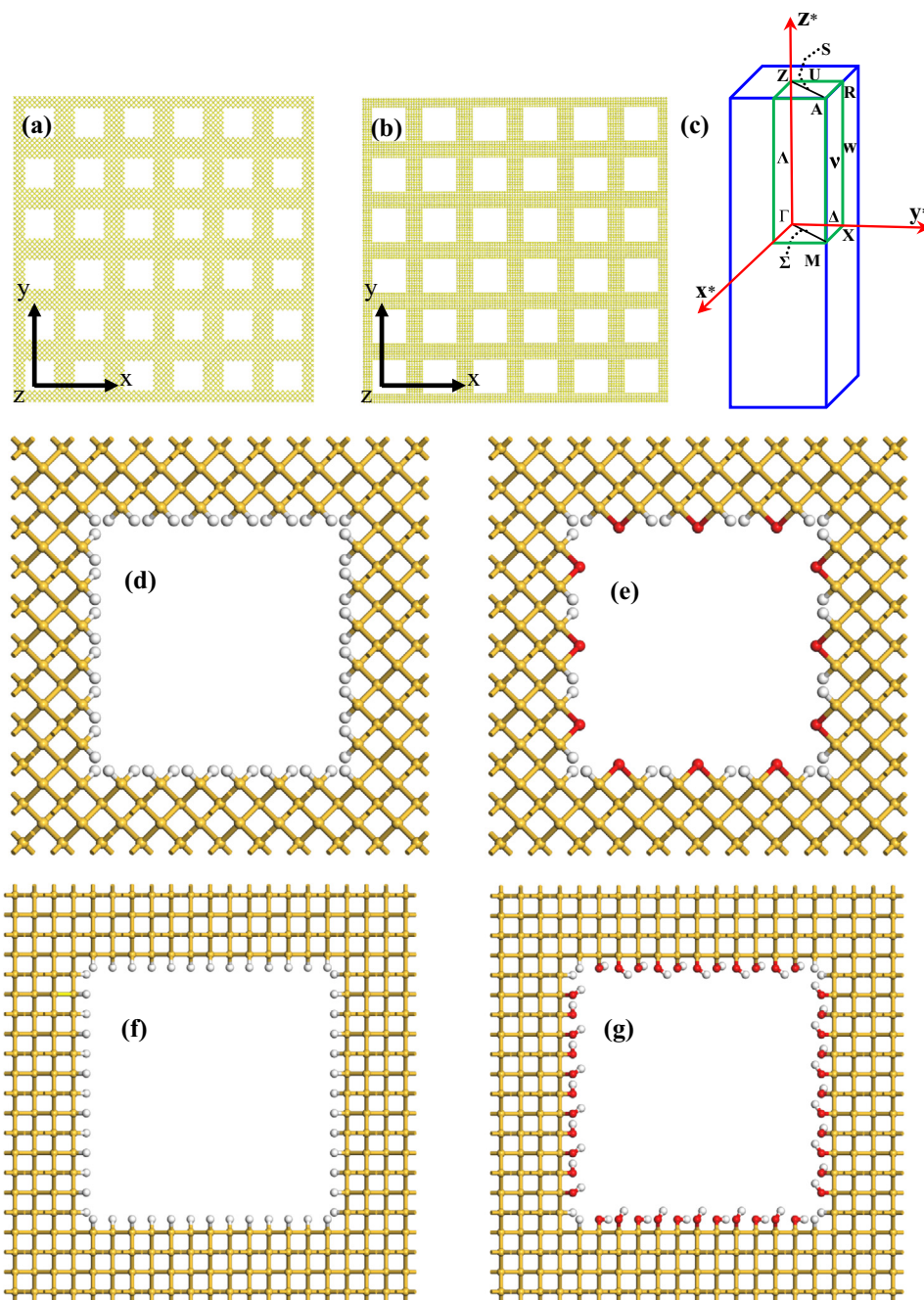

Fig. 1. Atomic structures and FBZ schemes of the silicon-based nanostructures. (a) [1 0 0] PS structure; (b) [1 1 0] PS structure; (c) FBZ of tetragonal crystal system; (d) 100P49TH; (e) 100P49TO; (f) 110P49TH; (g) 110P49TO. The yellow balls are Si. The gray balls are H and the red balls are O. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)