## Comment on "Valence Surface Electronic States on Ge(001)"

In a recent Letter [1], Radny *et al.* studied the ground state Ge(001) electronic structure near $E_F$ and claimed that the top of the valence band arises solely from back bond surface states. In this Comment, we show the following: (i) The top of the valence band of the Ge(001)-$c(4 \times 2)$ surface is not a back bond state, but a bulk state. (ii) The back bond state is ~0.4 eV below $E_F$ at $\Gamma$ and in resonance with the bulk state at $J$. Radny *et al.* estimated erroneously the position of the valence band maximum (VBM) and assigned the back bond state mistakenly. We found that the slab model with six atomic layers used in the density-functional calculation by Radny *et al.* is too thin to simulate the top valence band (TVB) dispersion near $E_F$.

We performed density-functional calculations using the VASP package as Radny *et al.* [1]. We employed a $c(4 \times 2)$ surface unit cell and calculated the band structures using slabs with different thicknesses. As the slab thickness increases from 6 to 16 atomic layers, the dispersion of TVB from $\Gamma$ to $J$ changes dramatically. For the slab with six or seven atomic layers, the VBM is found to locate at $J$, as shown in Fig. 1(a). Considering the Brillouin-zone folding, this VBM at $J$ corresponds to the VBM at $\Gamma$ in the band structure of the $a(4 \times 4)$ surface unit cell calculated by Radny *et al.*. However, the VBM moves to $\Gamma$ when the slab contains more than seven atomic layers [e.g., Fig. 1(b)]. The energy at $J$ of TVB decreases compared to that at $\Gamma$ with increasing slab thickness. So the slab model should contain at least eight atomic layers to describe the VBM correctly.

Figure 1(b) shows the band structures calculated using a ten-layered slab. The charge density of TVB near $\Gamma$ shows clear bulk state characteristics [see Fig. 1(c)]. This is consistent with the results of photoemission study by Nakatsuji *et al.* [2]. On the other hand, a state at ~0.4 eV below $E_F$ at $\Gamma$ is found to have exclusively back bond characteristics. As shown in Fig. 1(d), its charge density of near $\Gamma$ distributes dominantly at the back bond position of Ge dimers. Its energy increases from $\Gamma$ to $J$ and gets close to TVB near $J$. The charge densities are found to be mixed together near $J$ [as indicated by half-filled circles in Fig. 1(b)] between the TVB bulk state and the back bond state, showing distinct resonance characteristics. The TVB at $J$ is recognized as a surface resonance, located at ~0.1 eV below $E_F$. This state, together with the mixed state between the dangling bond $\pi$ state and the bulk state [indicated by half-filled squares in Fig. 1(b)] at ~0.2 eV below $E_F$, can well explain the unsigned scanning tunneling spectra feature at $\sim -0.1$ V seen by Gurlu *et al.* [3]. For the band structures calculated using the six-layered slab in Fig. 1(a), the back bond state is found at ~0.3 eV below $E_F$ at $\Gamma$. Compared to the ten-layered slab case, this state has much stronger resonance with the TVB state at $J$, which makes the TVB have higher energy at $J$ than at $\Gamma$.

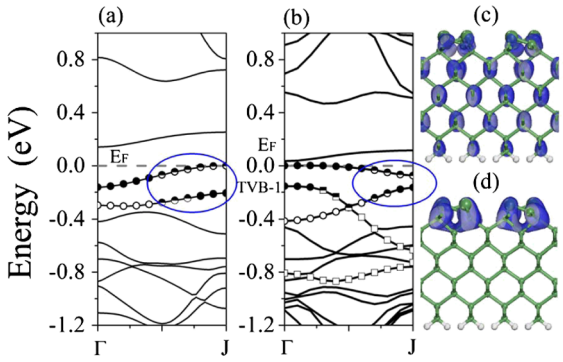


FIG. 1 (color online). The band structures from $\Gamma$ to $J$ of the Ge(001)-$c(4 \times 2)$ surface calculated using (a) a six-layered slab and (b) a ten-layered slab. The Fermi energy $E_F$ is set to zero and indicated by gray dashed lines. The filled black balls indicate the states with bulk derived features. The empty balls stand for the back bond state and the half-filled ones for the surface resonance between the back bond state and the bulk state. The big circle indicates the resonance region. The empty squares indicate the $\pi$ dangling bond state and the half-filled squares for the $\pi$ mixed with the bulk state. The charge densities of (c) the bulk state and (d) the back bond state at $\Gamma$ in band structure (b) are plotted on the right. The isosurface value is $6.0 \times 10^{-4}$ e/Å$^3$. The green balls stand for Ge atoms and white balls for H atoms.

Furthermore, using the ten-layered-slab, we simulated the filled state STM images for different bias voltage range. We also found the double lobed features in low-bias images and obtained good agreement with the experiments of Radny *et al.* [1].

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[1] M. W. Radny *et al.*, Phys. Rev. Lett. **100**, 246807 (2008).
[2] K. Nakatsuji *et al.*, Phys. Rev. B **72**, 241308(R) (2005).
[3] O. Gurlu, H. J. W. Zandvliet, and B. Poelsema, Phys. Rev. Lett. **93**, 066101 (2004).

 