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Observation of a possible superconducting gap in silicene on Ag(111) surface

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A possible superconducting gap, about 35 meV, was observed in silicene on Ag(111) substrate by scanning tunneling spectroscopy. The temperature-dependence measurement reveals a superconductor-metal transition in silicene and gives a critical temperature of 35–40 K. The possible mechanism of superconductivity in silicene is discussed. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4793998]

Silicon is the basis of current semiconductor industry regardless of emerging proposals that materials, such as diamond, carbon nanotube, or graphene, may replace silicon as the next generation semiconductors. It is of great interest if any new property could be found in this "old" material, since it will be easy for integration into the current semiconductor technology. For example, if silicon could be superconducting at reasonably high temperature, an era of "superconducting silicon industry" might immediately be foreseeable. Indeed, the discovery of superconductivity in boron doped diamond around 4 K,[1] and MgB_2 at 39 K[2] had stimulated great interest in the superconductivity in silicon-based materials, such as silicon carbide[3] or barium-doped silicon clathrates.[4] And soon it was found that highly boron-doped silicon is superconducting with a transition temperature (T_c) of 0.5 K[5] that is, however, too low to be of practical use. A route for increasing T_c is to find materials with strong electron-phonon coupling (EPC) contributing to the formation of Cooper pairs.[6] It was theoretically predicted that in 2D materials, like highly doped graphane, T_c higher than the boiling point of liquid nitrogen is possible.[7]

Silicene is a pure silicon sheet arranged in a honeycomb structure analogous to graphene.[8] It has attracted attentions because of the existence of Dirac fermion,[9] stronger spin-orbit coupling than graphene,[10] and compatibility with silicon-based nanotechnology. The Dirac fermion behavior of charge carriers in silicene on Ag(111) surface has been experimentally conformed recently.[11,12] In this Letter, we report the observation of a significant conductivity gap ($\Delta = 35$ mV) in silicene on Ag(111) surface. Several features, such as the precise location of the gap at the Fermi energy (E_F), the density of states (DOS) shoulders, indication of Andreev reflection, and gradual disappearance of the gap at temperature above 40 K, strongly suggest that it is a superconducting gap. The unusual high-T_c (about 40 K) superconductivity in silicene might result from the strong EPC and significant charge transfer from the Ag(111) substrate to silicene.

The experimental condition and sample preparation procedure were identical to that in Ref. 12. The dI/dV signals taken at 5 K were measured as the in-plane ac component in the tunneling current with a lock-in amplifier by superimposing a 2 mV ac voltage at 676 Hz on the given dc bias of the substrate-tip gap. Fig. 1(a) is an STM image showing a monolayer silicene film on Ag(111) substrate, running across several Ag(111) steps without losing continuity. As we described in Ref. 12, at liquid N_2 temperature (77 K), monolayer silicene exhibits a honeycomb structure with a periodicity of 0.64 nm (Fig. 1(b)), corresponding to $(\sqrt{3} \times \sqrt{3})R30°$ superstructure compared to the theoretical 1×1 silicene lattice. When cooled to liquid He temperature (5 K), silicene undergoes a phase transition. One of the two protrusions in each honeycomb unit cell becomes brighter than the other, showing a rhombic $(\sqrt{3} \times \sqrt{3})R30°$ superstructure (Fig. 1(c)). As there are two possible configurations, the surface is phase separated into triangular domains with either one of the two symmetric configurations. Two neighboring domains are separated by narrow boundaries where the neighbor protrusions are equally bright (Fig. 1(c)). The phase transition can be described by a "super-buckling model."[13] It has been known that free-standing silicene maintains a non-planar, so-called low-buckled (LB) geometry. When silicene is adsorbed on Ag(111) surface, it further adopts two mirror-symmetric $(\sqrt{3} \times \sqrt{3})R30°$ rhombic super-buckled structures. The low transition barrier between these two phases enables dynamic flip-flop motion at high temperature, resulting in the $(\sqrt{3} \times \sqrt{3})R30°$ honeycomb structure observed by STM.[13]

Scanning tunneling spectroscopy (STS) probes the local density of states (LDOS). Typical dI/dV curves over wide energy range (from −1.5 V to +1.5 V) obtained at 77 K and 5 K (Fig. 1(d)) reveal similar electronic structures: a small dip located at about 0.5 V attributed to the position of the Dirac point (DP) of silicene, and a pronounced peak at 0.9 V. The similar electronic structures of the two phases confirm that their basic structures are identical.

The dI/dV curve over a narrow energy range around Fermi energy (E_F) (from −120 mV to 120 mV) is substantially different at 5 K, as shown in Fig. 2(a). The spectra obtained on silicene shows a characteristic gap centered exactly at E_F and two significant shoulder peaks at both sides, while the spectra taken on Ag(111) do not exhibit any gap signature at E_F. Thus, the gap is not induced by the Ag(111) substrate or STM tip. These observations have been reproduced on many different monolayer silicene films, with different tips. We also measured STS spectra on different

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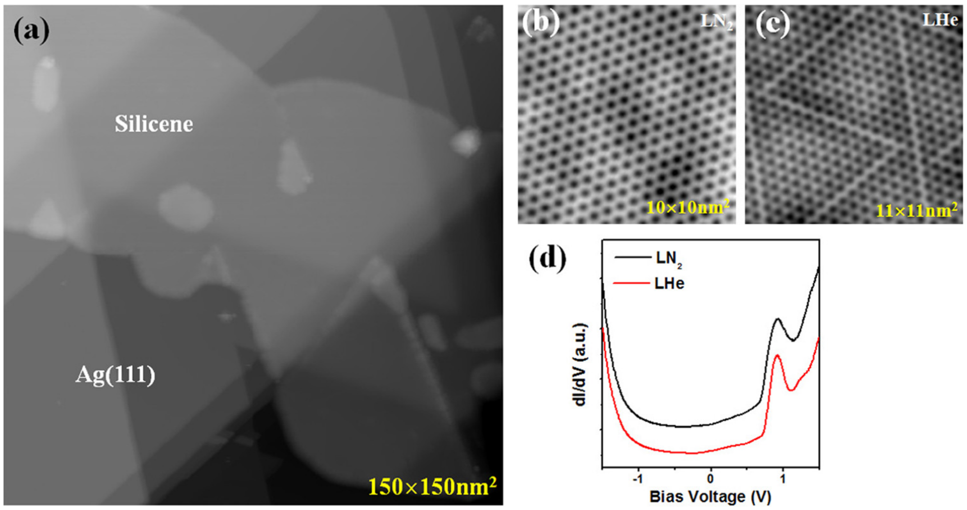

FIG. 1. (a) STM image of a monolayer silicene film on Ag(111) substrate, running across several Ag(111) steps. (b) and (c) High resolution STM images of silicene taken at tip bias 1.0 V at 77 K and 5 K, respectively. (d) dI/dV curves taken at 77 K (black curve) and 5 K (red curve), showing overall similar behavior (except the zero-bias gap which is too small to show in this voltage range). The curves are vertically shifted for clarity.

locations of the silicene surface and found that the gap exhibits high spatial homogeneity, as shown in Fig. 2(b).

The phenomenon that an energy gap opens at E_F is usually explained by following mechanisms: (I) phonon-mediated inelastic tunneling or Kondo effect; (II) Peierls transition; and (III) superconductivity. The gap induced by phonon-mediated inelastic tunneling in graphene can be as large as one hundred meV, but there are no DOS peaks on both sides of the gap.[14] Similarly, there are also no peaks on the both side of the gap induced by Kondo screening in Kondo lattice, for example, O_2 monolayer on Au(110) surface.[15] So the mechanism (I) is ruled out. Second, if the structural phase transition of silicene observed in our experiments (Figs. 1(b) and 1(c)) is a Peierls transition,[16] a gap should open at the DP of silicene, not around E_F (The DP is at 0.5 eV below E_F due to the charge transfer from Ag(111) to silicene). Moreover, we have shown that the phase transition in silicene is a dynamic phase transition, and not a Peierls transition.[13] Therefore, the mechanism (II) is also ruled out.

Therefore, we believe that the gap should be a superconducting one, and the two peaks are coherence peaks. We note the intensity of LDOS in the gap region does not go to absolute zero. This might be a result of the finite sample temperature in our experiments, which is not low enough. The temperature sensor in our STM system is a bit far from the sample, so the error of sample temperature measurement can be about several Kelvin. The intensity of LDOS in the gap can also be influenced by the DOS of Ag(111) substrate.

To confirm the observed superconductivity, we explored the superconductor-metal transition by varying the sample temperature. A sequence of dI/dV curves measured over the same monolayer silicene island at different temperatures (Fig. 2(c)) shows that the coherence peaks can be clearly observed up to 28 K. When the temperature is increased to 33 K, the superconducting gap is still observable, but the two coherence peaks start to disappear. The gap is no longer visible at 40 K, and the dI/dV curve reveals the metallic behavior without any gap. Such critical temperature (35 K∼40 K) is the highest among all other single-element superconductors discovered

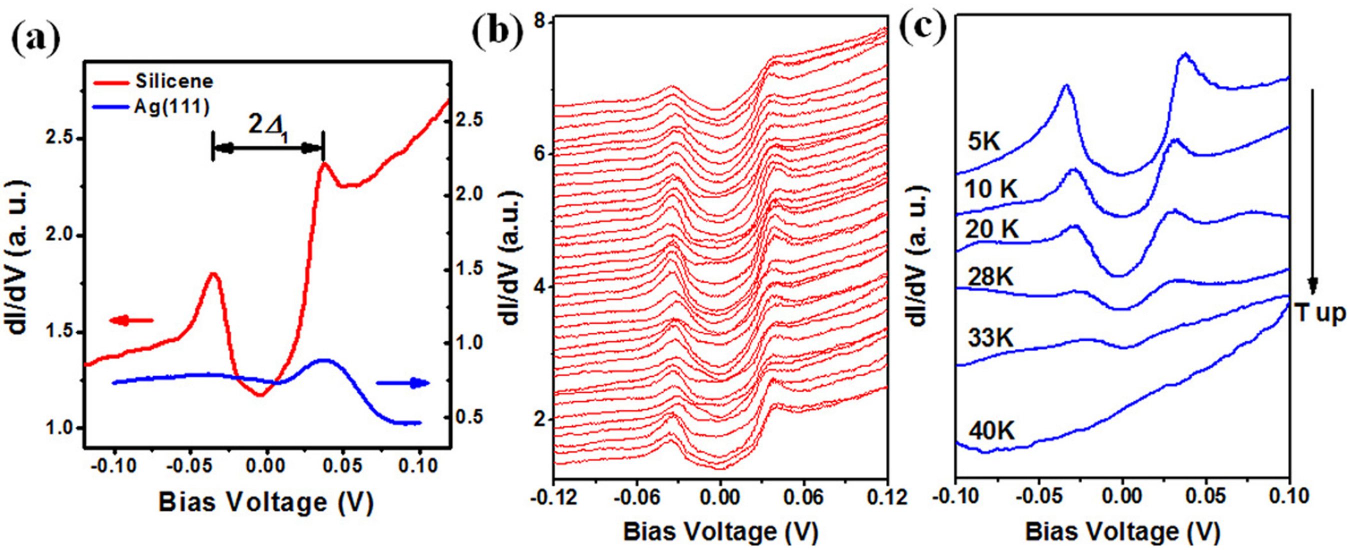

FIG. 2. (a) dI/dV curves obtained on silicene (red curve) and Ag(111) substrate (blue curve), respectively. (b) A series of dI/dV curves taken along a 15 nm line on silicene film, illustrating the uniformity of the gap. (c) Temperature dependence of dI/dV curve at same silicene film. The curves in (b) and (c) are shifted vertically for clarity.

so far, no matter they are 2D or 3D materials. The robust superconducting gap $\Delta_1 = 35\,\text{mV}$, which is half of the energy between the two coherence peaks, is much larger than conventional BCS superconductors, such as Nb,[17] $NbSe_2$,[18] and even MgB_2,[19] and comparable with high-temperature superconductors such as cuprate superconductors.[20] Considering that T_c is smaller than 40 K in this case, the $2\Delta_1/kT_c$ value is ~20 for this system, which is much larger than the BCS value of 3.52. If superconductivity is confirmed, then silicene on Ag(111) would unlikely be a conventional BCS superconductor. The dI/dV around the center of the gap (near E_F) exhibits V shape rather than U shape, which implies either the sample temperature is not low enough or it does not have an *s* wave pairing symmetry.

The honeycomb structure of silicene is similar to the B layer in MgB_2 and to graphene. The high T_c of conventional superconductor MgB_2 mainly stems from the strong electron-phonon coupling and the large charge transfer from Mg atoms to B layer.[21] The same mechanism has been applied to propose a superconductor of doped graphane with a T_c above the boiling point of liquid nitrogen.[7] In the case of silicene, the sp^3 hybrid electronic states have σ characteristic. These σ states are localized in the middle of the Si-Si bonds, and they should couple considerably to bond-stretching phonons. Furthermore, the buckling degree of Si atoms in $(\sqrt{3} \times \sqrt{3})R30°$ phase on Ag(111) (1.2 Å higher than lower layer of Si atoms[13]) is much higher than LB model of free standing silicene (0.4 Å),[9] which may increase the σ character in Si-Si bonds and result in the stronger electron-phonon coupling. The fact that the DP of silicene is at 0.5 eV below E_F reveals significant charge transfer from Ag(111) surface to silicene, which results in large density of electronic states at E_F. These two factors might work together to establish high temperature superconducting states in silicene, with $T_c \approx 35–40\,\text{K}$. Although silicene on Ag(111) may not be a conventional BCS superconductor, electron-phonon interaction may still play an important role in electron pairing.

We have performed STS measurements at different tip heights (smaller tunneling resistance means that the tip is closer to the surface), as shown in Fig. 3. When the tip approaches the surface, the tunneling conductance in the middle of the gap region is lifted, consistent with expected Andreev reflection[22] in this superconductor-metal junction. This provides another evidence of superconductivity in silicene. Another finding is the emergence of a smaller gap around E_F with $\Delta_2 = 15\,\text{mV}$ when the tip gets close to the surface, which implies that silicene on Ag(111) surface may be a two-band superconductor, similar as MgB_2.[21] Another possibility is that the smaller gap may be results from the proximity effect. However, these features still need further confirmation, due to the finite cooling temperature and thus limited energy resolution in our system.

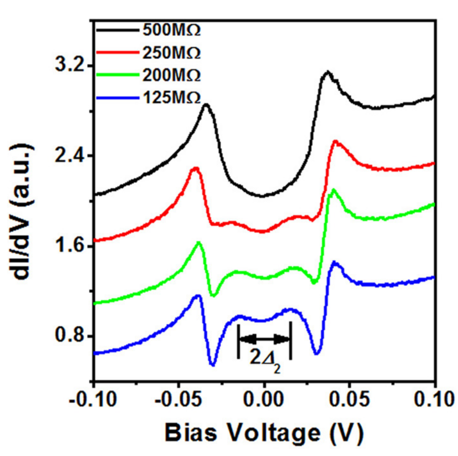

FIG. 3. dI/dV curves taken at different tunneling resistance of tunneling junction formed between STM tip and surface. The curves are shifted vertically for clarity.

In summary, we have observed a possible superconducting gap in silicene on Ag(111) surface. The critical temperature of 35–40 K is higher than all other single-element superconductors discovered so far. Though we believe that the strong electron-phonon coupling in silicene plays an important role in the formation of superconducting phase, the fundamental understanding of superconductivity in silicene, such as pairing mechanism and pairing symmetry, is still unknown and need to be investigated.[23] A transport measurement is currently under investigation in order to provide a direct proof of the superconductivity. However, challenges including the oxidation of silicene in air and the high conductivity of the Ag substrate still need to be overcome.

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