Ultrafast dynamics in epitaxial silicene on Ag(111)

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Abstract: Ultrafast transient reflectivity measurements were performed in epitaxial 4x4 silicene grown on Ag(111). Comparison with bulk silicon and silver response highlighted the occurrence of peculiar photo-physical mechanisms, suggesting a metallic-like behavior in silicene.
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A 2D honeycomb crystalline form of silicon, the so called "silicene", has recently attracted great attention as a novel graphene-like material [1]. Until now, free standing silicene has never been observed, because a 2D sp^2 Si crystal is chemically unstable in ambient conditions [2]. Nevertheless, quasi-two dimensional honeycomb Si layers grown by molecular beam epitaxy can be stabilized by a supporting substrate, as shown in recent pioneering experiments [3]. To date, buckled silicene structures have been experimentally reported on substrates with metallic character, including Ag(111) [4,5], Ir(111), [6] and ZrB_2 [7].

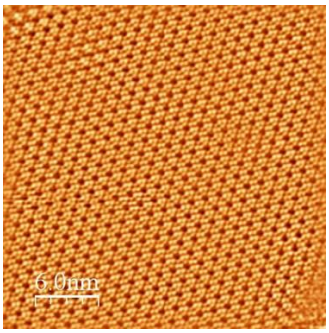

Figure 1 STM image of the silicene sample

Despite huge efforts devoted to the characterization of epitaxial silicene by means of STM/STS, LEED and ARPES, an unambiguous picture of its physical properties is still lacking. Indeed the presence of degenerate surface superstructures together with a partial hybridization between Si and Ag atoms makes the valence band structure of the epitaxial silicene non-trivial, hence providing controversial interpretations [4, 8, 9].

Here we present a study of ultrafast transient reflectivity in 4x4 silicene superstructure grown on Ag(111) and capped with Al_2O_3 [10]. We compare the results with measurements performed in bulk silicon, on the silver substrate and on oxidized silicene. We observed a substantial difference in the silicene response with respect to the other samples considered, confirming the presence of a peculiar electronic dynamics that suggests a metallic-like behavior similar to the one reported in graphene [11].

Figure 1 shows the STM image of the 4x4 silicene superstructure on Ag(111) as the one investigated in the experiments. The honeycomb nature of the silicene lattice has also been confirmed by multi-wavelength resonant Raman spectroscopy supported by ab initio calculations [12]. The ultrafast photo-physical properties of silicene were investigated by performing pump-probe measurements in reflection geometry with a temporal resolution of about 20 fs. We used as a probe the second harmonic of a visible optical parametric amplifier (OPA) [13] in order to achieve a pulse duration of approximately 20 fs in the probe region from 340 nm to 370 nm. We excited the sample with a broadband visible pulse, spectrally peaked around 500 nm, obtained from another OPA. Both the two OPAs were driven by an amplified Ti:sapphire laser system (500 μJ, 150 fs, 1 kHz). After chirped mirror compression, the duration of the pump pulse was less than 15 fs. We measured the probe reflection of the sample with an optical multichannel analyzer working at the full repetition rate of the laser source. The acquisition of the pump-perturbed and pump-unperturbed probe spectra allowed extraction of the sample differential reflectivity $\Delta R/R$.

The results are shown in figure 2 where the sample reflectivity is reported as a function of the pump-probe delay and probe wavelength. Panel (a) and (b) correspond to the Ag(111) substrate and oxidized silicene respectively. A very similar fast signal is observed around zero delay in both measurements. This could be attributed to the ultrafast response of silver. Indeed the oxidation process transforms the silicene in silicon oxide, which does not contribute to the transient reflectivity of the sample because of the strong increase of the optical gap due the oxidation process (9 eV). Panel (c) shows the reflectivity change in bulk silicon. One can see a decrease of reflectivity which takes place in the first 200 fs followed by a very slow recovery on the scale of tens of picoseconds; this is consistent with early studies on the ultrafast response of silicon [14].

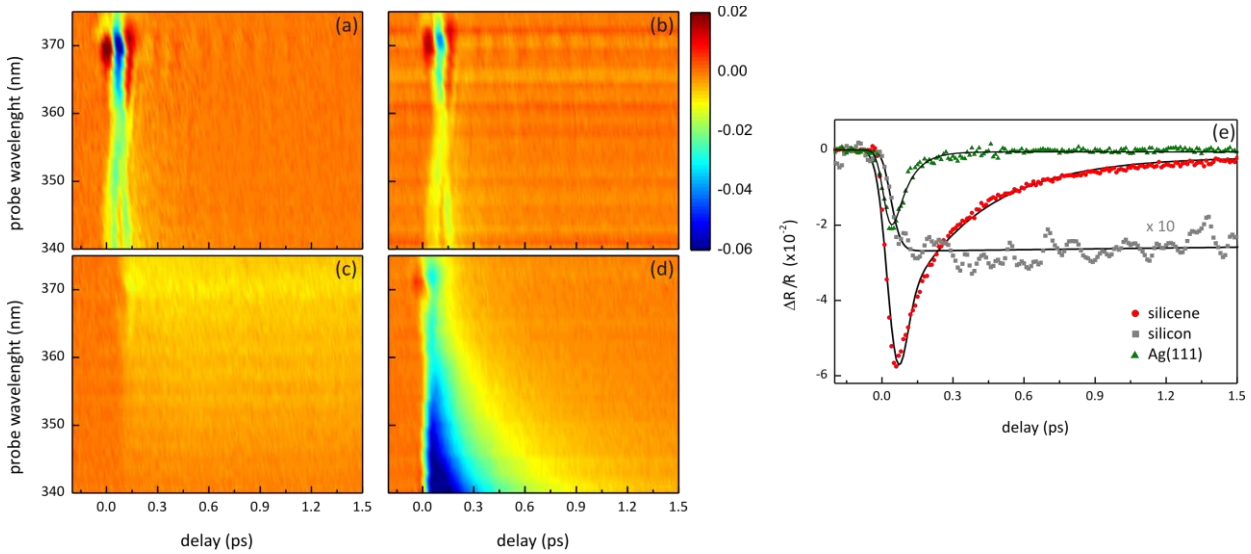

Figure 2 Transient reflectivity change as a function of pump-probe delay and probe wavelength in (a) Ag(111), (b) oxidized silicene on Ag(111), (c) bulk silicon and (d) silicene on Ag(111) with Al_2O_3 capping layer. (e) Transient reflectivity change as a function of pump-probe delay for the probe wavelength of 350 nm in silicene (red dots), bulk silicon (grey squares, signal multiplied by 10) and Ag(111) (green triangles). Solid lines are fits by multi-exponential decay convoluted with the instrument response function.

The result of pump-probe measurement in silicene is reported in figure 2 panel (d). We observed a very intense feature in the ΔR/R spectrum followed by a fast recovery on the picosecond timescale. Figure 2 (e) reports the transient reflectivity change corresponding to the probe wavelength of 350 nm for silicene (dots), bulk silicon (squares) and the silver substrate (triangles). The difference among the response of the samples is very clear. A multi-exponential fit is reported as a solid curve for each sample in figure 2 (e). The fit gives a recovery time of 65 fs for the silver substrate, that corresponds to the very fast electron relaxation occurring in metals. On the other hand, bulk silicon shows a slow recovery with a time constant of 35 ps. This can be attributed to the energy gap that hinders the electron-hole recombination in a semiconductor like silicon. In the case of silicene, the signal presents two components with time constant of 166 fs and 860 fs. These fast time constants suggest the metallic-like nature of this material.

In conclusion, we reported ultrafast reflectivity measurements in 4x4 epitaxial silicene grown on Ag(111). The experimental results show peculiar characteristics which cannot be ascribed to the silver substrate and that are substantially different from the bulk silicon response. These results contribute to the understanding of silicene physical properties, suggesting a metallic-like behavior in the 4x4 superstructure.

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