Controlled assembly of graphene-capped nickel, cobalt and iron silicides

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The unique properties of graphene have raised high expectations regarding its application in carbon-based nanoscale devices that could complement or replace traditional silicon technology. This gave rise to the vast amount of research on how to fabricate high-quality graphene and graphene nanocomposites that is currently going on. Here we show that graphene can be successfully integrated with the established metal-silicide technology. Starting from thin monocrystalline films of nickel, cobalt and iron, we were able to form metal silicides of high quality with a variety of stoichiometries under a Chemical Vapor Deposition grown graphene layer. These graphene-capped silicides are reliably protected against oxidation and can cover a wide range of electronic materials/device applications. Most importantly, the coupling between the graphene layer and the silicides is rather weak and the properties of quasi-freestanding graphene are widely preserved.

For almost ten years, graphene, a two-dimensional crystal of carbon atoms packed in a honeycomb structure, has been in the focus of intensive research. Its remarkable and promising electronic properties have raised high expectations regarding its potential use in the next generation electronics of a post-silicon era. However, a graphene-based technology first and foremost requires reliable and low-cost approaches to fabrication of high-quality and large-scale graphene layers on a variety of functional substrates. A major challenge is the integration of graphene into the current Si-based technology, for which original solutions have become available recently. One basic idea is to use silicon to create a semiconducting or an insulating buffer between graphene and a metallic substrate, and thus to obtain structures that are suitable for electronic applications.

We propose to use monocrystalline films of nickel, cobalt and iron as the substrates, on top of which high-quality graphene can be easily created using the Chemical Vapor Deposition (CVD) approach. The silicides of these three metals in particular exhibit a variety of functional properties and are already extensively used. It is worth noting that metal silicides are generally currently employed for many applications including complementary metal oxide semiconductor (MOS) devices, thin film coatings, photovoltaics, thermoelectrics, catalysts and biomolecule sensing.

For instance, the use of Ni silicides as metal gate electrodes in complementary MOS devices has attracted particular attention. Ni-rich silicides, like Ni5Si3, Ni3Si and Ni33Si12, can be used for p-MOS gates due to their higher work function, while NiSi, Ni5Si3 and Ni3Si are attractive for n-MOS applications. Ni and Co silicides also exhibit intriguing electronic properties, especially in the form of nanowires or nanobelts. The compound CoSi2, similarly to Ni silicides, is a material of choice to contact the source, drain and gate areas in complementary MOS devices. The quite different electronic and magnetic properties of Fe-based silicides ensure huge potential of these materials for various applications, too. For example, α-FeSi2 exhibits metallic properties while β-FeSi2 is a narrow-gap semiconductor. Ferromagnetic Fe3Si layers can be used as a source for injection of spin-polarized electrons into a semiconductor.

The aim of this work is to uncover the basic properties of the graphene/silicide interfaces. Here, we demonstrate that intercalation of silicon atoms underneath the graphene top layer and a series of annealing cycles allow one to create a variety of metal silicides with different properties, all nicely covered and protected by graphene. The graphene layer itself barely interacts with the silicides underneath and shows quasi-freestanding character. We anticipate a wide range of opportunities where the properties of such silicides, the graphene layer on top of the semiconducting silicides or of both combined could be utilized.
**Results**

Fig. 1 schematically illustrates the proposed approach. In the beginning, a high-quality and large-area graphene layer is CVD-grown on a single-crystalline thin Ni, Co or Fe film substrate. Then, silicon atoms are gradually deposited on top of the freshly prepared graphene layer. Their penetration underneath graphene occurs already at room temperature (RT). The mechanism of such intercalation process is based on the well-known fact that graphene grown on transition metal surfaces like Ni, Co, Pt, Ru etc. possesses a domain structure. Thus, the intercalation of different elements like Si or Au occurs via the domain boundaries\(^{38}\). Since the solubility of Si in Ni is relatively high and the diffusion barrier for the deposited atoms on graphene is evidently quite low, silicon atoms will migrate to these domain boundaries and penetrate underneath graphene already at room temperature. In order to promote the chemical reaction between Si and metal, and obtain the desirable silicide phase, subsequent annealing cycles must be applied. The stoichiometry of the metal silicides can be controlled by the quantity of intercalated silicon as well as the duration and temperature of the annealing procedure. The silicon intercalation also considerably attenuates the strong hybridization between the electronic states of graphene and the substrate and, in particular cases, leads to the stabilization of the properties of quasi-free-standing graphene.

**Graphene on Ni-silicide structures.** We first go through the detailed analyses of the steps towards silicide formation in the case of Ni.

![Schematic illustration of the proposed approach.](image)

At first, graphene is produced by CVD on 10 nm-thick metallic films of Ni(111), Co(0001) or Fe(110) grown epitaxially on W(110). Then, cycles of silicon deposition and annealing are performed to promote intercalation of silicon atoms underneath graphene and initiate silicide formation. Desirable composition and properties of graphene-protected silicides depend on the amount of deposited silicon as well as temperature and duration of annealing.

**Figure 1** Schematic illustration of the proposed approach. At first, graphene is produced by CVD on 10 nm-thick metallic films of Ni(111), Co(0001) or Fe(110) grown epitaxially on W(110). Then, cycles of silicon deposition and annealing are performed to promote intercalation of silicon atoms underneath graphene and initiate silicide formation. Desirable composition and properties of graphene-protected silicides depend on the amount of deposited silicon as well as temperature and duration of annealing.

**Figure 2** Revealing the early stages of Si intercalation and silicide initiation on Ni substrate. The sequence of C 1s and Si 2p core level spectra for graphene/Ni(111) (a), and with increasing doses of Si deposited on top, accompanied by annealing treatments (b–f). The highlighted part of the C 1s spectra is associated with decoupled graphene regions. 1 Å corresponds to the Si coverage of 2.88·10\(^{14}\) at/cm\(^2\). The C 1s and Si 2p spectra were taken with 470 eV and 135 eV photons, respectively.
Fig. 2 shows the core-level photo electron (PE) spectra of graphene freshly prepared on Ni(111), after deposition of small doses of silicon atoms, and after the post-annealing treatment. The C 1s spectrum of native graphene/Ni at the bottom of the left panel looks very similar to that previously reported for this system. Even a small dose (~6 Å) of silicon deposited at RT notably changes the spectral shape and gives rise to a shoulder at lower binding energies (BE). The Si 2p spectrum does not reveal a well-resolved spin-orbit doublet. Instead, we see a rather extended and unshaped bump feature at the BE of ~99.3 eV, which is consistent with the reported values for Si 2p_{3/2} of clean silicon (which is 98.9–99.6 eV depending on the surface reconstruction type). Together with a blurred LEED pattern (not shown) in comparison to that obtained from native graphene on nickel, these observations suggest that the major amount of the deposited silicon atoms creates disordered, amorphous islands on top. However, the shoulder in the C 1s spectrum at 284.5 eV implies that the penetration of silicon underneath graphene already starts at RT, and graphene is already partly lifted up and detached from the substrate.

Annealing of this structure at 450°C for 40 minutes almost restores the shape of the C 1s spectrum. At the same time, it leads to complete disappearance of the bump feature and the formation of a well-resolved Si 2p spin-orbit doublet. The BE of the Si 2p_{3/2} component is 99.5 eV, which is in a good agreement with the known values for nickel silicides. Compared to the spectrum before annealing the Si 2p intensity became notably smaller and the LEED pattern again reveals a sharp (1 × 1) hexagonal structure with low background.

Hence, the post-annealed state may be described as complete intercalation of silicon atoms underneath graphene. One may assume that due to their notable diffusion and relatively high solubility in nickel, the majority of Si atoms penetrate deep into the bulk of the substrate, thus becoming undetectable by XPS. This could reasonably explain the drop in the PE intensity of the Si 2p spectrum. The restored shape of the C 1s spectrum suggests that the chemical interaction of graphene with the underlying silicon-containing nickel substrate is similar to what was found for the native graphene/nickel system. Essentially, the intercalation of silicon atoms under graphene and their diffusion deeper into the Ni film leads to the formation of a Ni-Si solid solution in the subsurface region with a Si concentration up to the solubility limit of about 10 at.%. Further increase of the Si concentration should give rise to Ni silicide formation starting from the Ni_{3}Si phase. Thus, the Ni silicide formation should be steered by the balance of the intercalation rate and the bulk diffusivity.

Upon depositing further portions of silicon at RT and subsequent post-annealing processes, the system strictly follows the scenario described above. The Si 2p spectrum taken immediately after the Si deposition reveals again a bump-like structure showing that plenty of amorphous silicon islands are formed on top of the graphene layer. Its PE intensity decreases considerably after the annealing cycles, and gradually, the well-resolved Si 2p doublet becomes dominant. The latter, apparently, originates from the ordered phases of intercalated Si atoms in nickel. This time longer annealing at higher temperature, 500°C, does not completely remove the bump in the Si 2p spectrum. This may be explained by the formation of oxidized silicon islands.
which were not intercalated under the given conditions. Clearly, the substrate becomes richer in silicon, implying the formation of the silicide phases underneath graphene. The LEED picture taken after the last treatment, corresponding to the upper PE spectra in Fig. 2, now reveals a sharp (2 × 2) structure with respect to the Ni(111) surface. The stoichiometry of the formed silicide will be discussed below.

The evolution of the system with increasing deposited, and subsequently intercalated silicon, up to 34 Å of nominal thickness, is shown in Fig. 3. The series was measured on a freshly prepared graphene/nickel substrate. Each annealing step was done for 10 min and at a temperature of 430 °C.

This time, the shoulder at the lower BE in the C 1s spectrum shaped into a well-defined peak at 284.5 eV. It is worth noting that we do not detect any sign of a PE signal at 283 eV BE which would be indicative of carbide phases, i.e. degradation of the graphene layer. It is interesting to compare the C 1s spectra depicted in Fig. 2e and Fig. 3b, as the amount of deposited silicon in these two experiments was the same but the annealing temperatures are different. Apparently, reducing the temperature as well as the duration of annealing effectively increased the amount of silicon in the subsurface region underneath graphene. This is reflected in the C 1s spectrum as a noticeable enhancement of the PE intensity at 284.5 eV.

The LEED picture again reveals a sharp (2 × 2) pattern. Taking into account the silicon concentration estimated from the Si 2p/Ni 3p intensity ratio we suppose, that such structure corresponds to the formation of ordered Ni3Si silicide under graphene. The solid state diffusion and the formation of a bulk alloy rather than a surface compound is supported by the fact that Si concentration decreases after annealing. This process is quite similar to the recently observed formation of the bulk Ni3Al phase with a (2 × 2) surface structure as a result of graphene intercalation with Al atoms. The possible structural model is shown in Fig. SI. The Si 2p spectral shape becomes very different from that of the Si-depleted systems described above. We see now a new well-defined peak at lower BE. To gain insight into the spectral structure of the discussed Si 2p core-level spectrum, we recorded it at two different photon energies, 165 eV and 420 eV, and then deconvolved the obtained Si 2p spectra as shown in the right panel of the Fig. 3.

Both PE spectra were normalized to the maximum intensity. Each spectrum can be fitted with two doublets, where the two components likely reflect electron emission from Si atoms in the subsurface and in the bulk. The lower BE component is enhanced at the lower photon energy, which allows it to be assigned to the surface structure. Hence, the higher BE component originates from silicon atoms embedded in the bulk of the system.

We analyzed the Si 2p/Ni 3p intensity ratio at each stage in order to evaluate the stoichiometry of the formed structure and to follow its evolution during the experiment. The obtained data together with the well-known phase diagrams for the Ni-Si system suggest that starting from the solid solution we have passed from the Ni-rich phase Ni3Si to NiSi. We have to admit that there may be a certain gradient of the silicon concentration from the surface to the bulk. Thus, for each particular system we may have several Ni-silicide phases with higher Si concentration at the near-surface region, which is probed with XPS and solely defines the properties of the graphene-silicide interface. It should be noted that at low dosage of the intercalated silicon the multicomponent structure of the C 1s
spectrum indicates coexistence of the graphene/silicide and graphene/nickel interfaces.

In Fig. 4, we show the evolution of NEXAFS C-K edge spectra, which allows us to follow possible modifications of the $\pi$ and $\sigma$ electronic states of graphene with increasing intercalated Si. The shape of the C-K edge spectrum of freshly prepared graphene on Ni(111) has been intensively discussed recently. It contains two characteristic features, a double peak at $285 \text{ eV}$ and a manifold structure at $292 \text{ eV}$. They reflect C 1$s$ core electron excitations into the $\pi^*$ and $\sigma^*$ states, respectively. Both features are substantially broadened compared to what is observed for quasi-freestanding graphene because of the strong hybridization between the electron states of carbon and nickel. The red-colored parts of the spectra do not show the strong angular dependence typical for the $\pi^*$ and $\sigma^*$ features. This suggests that the sp$^2$ character of the $\pi$ states is altered due to the interaction with the Ni atoms below. Upon the transition from the solid solution via Ni-rich phases to the NiSi silicide, the lineshape of the spectrum becomes more and more similar to that of the freestanding graphene. This suggests that with increasing amount of silicon atoms inside nickel, the Ni 3$d$ states participate more actively in the formation of the Ni-Si bonds in silicides and, in turn, interact less and less with graphene. As a result, the electronic coupling between the graphene and the silicide substrate becomes weak.

Graphene on Co- and Fe-silicide structures. Having established a clear picture of the formation of Ni-silicides under CVD-grown graphene, let us now turn to a brief description regarding Co- and Fe-based systems.

We performed the experiments in the same way and deposited first the silicon atoms on top of the freshly prepared graphene layer on monocrystalline films of cobalt or iron at RT. Later on, the annealing cycles were applied and the full process was monitored by analyzing the C 1$s$ and Si 2$p$ spectra, which are depicted in Fig. 6 and Fig. 7, respectively. The stoichiometry of the metal-Si systems was evaluated via the Si 2$p$/Co(Fe) 3$p$ ratio.

Discussion

Looking closely at the presented spectra, we may see and discuss certain similarities as well as differences of the silicide formation in these three systems. We should note that the silicide formation is solely defined by the local subsurface Si concentration, which, in turn, is governed by the balance of intercalation and diffusion rates. The local concentration of silicon atoms should be higher than that defined by the silicide stoichiometry, for example, not less than 50 at.% for NiSi. Both diffusion and intercalation rates increase with
temperature, these dependencies are described by Arrhenius equations with two different activation energies. The choice of the heat treatment temperature and duration can be performed using these equations. Unfortunately, the lack of fundamental information on this matter allows us to explain the behavior of these three systems on the phenomenological level only.

Despite the fact that Ni and Co metals exhibit very similar properties, the difference in the behavior of graphene/Ni and graphene/Co systems upon Si intercalation can be explained as follows: the Ni$_3$Si phase exists in a wide temperature range in the Ni-rich part of the Ni-Si system. In contrast, the Co$_3$Si phase is observed only within a short range of relatively high temperatures. The Ni$_3$Si phase has a similar crystal structure to Ni, i.e. it arises due to the ordering in Ni-Si solid solution. In such systems typically the interactions between different atoms are stronger than for the atoms of the same element. This enhanced interaction, in turn, promotes interdiffusion due to thermodynamic reasons. Because of this, the Si diffusion in Ni is notably faster than that in Co in the corresponding metal-rich solid solutions. Therefore, in the Co-based systems the surface-related component of the Si 2p spectrum always has higher intensity than the bulk one, which is not the case for the Ni-based structures. Note that for Fe-based systems this situation becomes somewhat intermediate, because similar to Ni, Fe forms extended solid solutions with Si up to the ordered intermetallic phases Fe$_3$Si. Hence, the discussion given above is true for the graphene on iron system, too. However, in contrast to nickel, iron has a higher melting point. Therefore, the bulk diffusion is activated at essentially higher temperature. Thus, at the same temperature, Si evidently has higher diffusivity in nickel crystal than in iron one. This is in line with our spectral observations described above.

In summary, we have demonstrated that the ordered silicides of Ni, Co and Fe with different and well-defined stoichiometries can be produced under CVD-grown graphene. The obtained materials are reliably protected by the graphene layer, making them compatible for a variety of nanoscaled applications at ambient conditions. Our findings suggest that the graphene layer is weakly electronically coupled to the silicide phases, thus keeping its remarkable properties ready for use. We anticipate that the presented results will create a solid platform to further explore the opportunity to integrate graphene with the mature silicon-based technology. We believe that this would give rise for further exploitation of the unique properties of different metal silicides under graphene’s umbrella as well as the properties of graphene itself for the widely discussed applications in the next-generation electronic devices.

**Methods**

The studied graphene samples were synthesized in situ by CVD from propylene (C$_3$H$_6$) on the Ni(111), Co(0001) and Fe(110) surfaces. For this purpose we prepared metallic films with a thickness of 10 nm grown epitaxially on the W(110) substrate in ultra-high vacuum conditions. The high crystalline quality of the studied samples was confirmed by the sharp low energy electron diffraction (LEED) patterns. After that, graphene layer was grown on nickel and cobalt surfaces at a pressure of propylene of ~10^-6 mbar and the substrate temperature of 600°C during 15 min. At these conditions the reaction is well-known to be self-limited to single graphene layer. The parameters of CVD for the iron-based system were slightly increased to avoid carbidization and produce a complete graphene layer, namely 5 x 10^-6 mbar, 700°C and 25 min, respectively (see Supplementary Note 1 for details). The penetration of the silicon atoms into the metal substrates and the subsequent formation of various types of silicides underneath the graphene top layer were studied using X-ray photoelectron spectroscopy (XPS), angle resolved photoelectron spectroscopy (ARPES), near-edge X-ray absorption fine structure spectroscopy (NEXAFS), and LEED. The well-known stability of graphene-based systems to ambient atmospheric conditions, these dependencies are described by Arrhenius equations with two different activation energies. The choice of the heat treatment temperature and duration can be performed using these equations. Unfortunately, the lack of fundamental information on this matter allows us to explain the behavior of these three systems on the phenomenological level only.

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conditions\(^{12,13}\) was proved for the studied structures, too. Experiments were performed at BESSY synchrotron radiation facility - at the beamlines U125/2-SGM, UE56/2-PCM-2 and at the Russian-German beamline. ARPES measurements were performed at room temperature with a Scienta U4000 spectrometer.

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Acknowledgements

This work was supported by BMBF (grant No. 05K1203D), RFBR (No. 11-03-00752) and St. Petersburg State University (No. 11.37.634.2013) grants. D.U., O.V. and A.F. acknowledge funding from the President’s grant MK-3303.2012.2. We acknowledge Helmholtz Zentrum Berlin für Materialien und Energie for support within bilateral Russian-German Laboratory program.

Author contributions

O.V., D.U. and D.V.V. designed the research. O.V., A.F., D.U., A.V.G., K.B. and A.G. have participated in XPS, NEXAFS and ARPES experiments. Operation of the XPS and ARPES facilities was carried out by O.V., A.F. and D.U. Theoretical modeling was performed by L.V.Y. and N.L.V. All authors discussed the results. The manuscript was written by O.V., L.V.Y., D.U. and D.V.V. All authors have read and approved the decisive version of the manuscript.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/srep.

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Vilkov, O. et al. Controlled assembly of graphene-capped nickel, cobalt and iron silicides. Sci. Rep. 3, 2168; DOI:10.1038/srep02168 (2013).

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