A review on silicene — New candidate for electronics

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ABSTRACT

Silicene – the silicon-based counterpart of graphene – has a two dimensional structure that is responsible for the variety of potentially useful chemical and physical properties. The existence of silicene has been achieved recently owing to experiments involving epitaxial growth of silicon as stripes on Ag(001), ribbons on Ag(110), and sheets on Ag(111). The nano-ribbons observed on Ag(110) were found – by both high definition experimental scanning tunneling microscopy images and density functional theory calculations – to consist of an arched honeycomb structure. Angle resolved photo-emission experiments on these silicene nano-ribbons on Ag(110), along the direction of the ribbons, showed a band structure which is analogous to the Dirac cones of graphene. Unlike silicon surfaces, which are highly reactive to oxygen, the silicene nano-ribbons were found to be resistant to oxygen reactivity.

On the theoretical side, recent extensive efforts have been deployed to understand the properties of standalone silicene sheets and nano-ribbons using both tight-binding and density functional theory calculations. Unlike graphene it is demonstrated that silicene sheets are stable only if a small buckling (0.44 Å) is present. The electronic properties of silicene nano-ribbons and silicene sheets were found to resemble those of graphene.

Although this is a fairly new avenue, the already obtained outcome from these important first steps in understanding silicene showed promising features that could give a new future to silicon in the electronics industry, thus opening a promising route toward wide-range applications. In this review, we plan to introduce silicene by presenting the available experimental and theoretical studies performed to date, and suggest future directions to be explored to make the synthesis of silicene a viable one.

Contents

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1. Introduction

A new crystalline silicon form the so called "silicene" – the silicon-based counterpart of graphene – moved up from theoretical predictions to experimental observations in just a few years. In this review we will discuss the present status of the experimental and theoretical studies on silicene.

Before we move on to the case of silicene, we very briefly bring in the case of graphene, which has attracted a worldwide attraction. There are several carbon structures among which the well-known are graphite and diamond. A stack of planar hexagonal structure composes the former and is very popular nowadays because it has been used to extract graphene sheet [1]. Graphene is only one-atom thick layer of sp^2-bonded carbon in a honeycomb crystal structure [2] and is probably the most investigated system in materials science during the last decade. It presents striking properties, which lead to potentially novel routes for many applications [2–4].

Silicon atoms, however, have similar electronic configurations as those of carbon. In general, the explanation of why carbon makes honeycomb structures and not silicon stems from the fact that the sp^2 hybridization is more stable than sp^3 hybridization for carbon but for silicon the situation is the reverse one [5]. It is hence energetically not favorable to form spontaneously silicene from silicon atoms.

Very recently, new silicon based structures have been discovered such as single and multi-walls nanotubes (NTs), which open the door to imagine that graphene-like silicon structures could be obtained using catalysts such as surfaces.

Since the discovery of graphene, theoretical studies using *ab-initio* level calculations [6,7] attempted to establish theoretical similarities between carbon NTs and hypothetical silicon NTs, such as band structure and density of states. Fagan et al. predicted that the electronic properties of single-wall silicon NTs are very similar to the equivalent carbon NTs [6]. From the experimental point of view, silicon tubular structures and NTs have been synthesized by different process [8–10], which raised the question of the existence of other crystalline forms of silicon, different from the well-known diamond structure.

Two-dimensional silicon nanostructures were probably first fabricated by solution-based methods. Thus, Nakano et al. made silicon sheets by chemical exfoliation of $CaSi_2$ [11]. Nevertheless, they were Mg-doped, had silicon bonded to oxygen, and were proposed to be $\langle 110 \rangle$ oriented. Tunneling electron microscopy (TEM) and atomic force microscopy (AFM) images revealed a hexagonal structure with atomic separations of about 0.41 nm. In order to obtain oxygen-free nanosheets, Okamoto et al. [12,13] performed exfoliation of layered polysilane by reaction with n-decylamine, leading to Si(111) planes with amines covalently bonded. In their study, Okamoto et al. reported that these nanosheets are "free-standing" with a thickness less than 2 nm. Time-resolved photoluminescence measurements with emission at 435 nm indicate that these nanosheets belong to the class of direct gap materials. Synthesis of silicon nanowires by chemical etching has also been reported as well [14].

In 2007, Guzmán-Verri and Lew Yan Voon developed a tight-binding (TB) Hamiltonian that takes into account the electronic properties of Si NTs and silicene [15]. These results show that silicene is semi-metallic. Subsequently, two other theoretical studies [16,17], using density functional theory (DFT), have shown that a silicon quasi-two dimensional structure is stable. Several others then followed these studies, which will be discussed in details in the present review. On the other hand, recent experimental studies explored the epitaxial adsorption of silicon on silver surfaces resulting in an evidence of the possible formation of silicene nano-ribbons (NRs) and sheets [18–25]. This has been supported by *ab initio* calculations for silicene NRs on Ag(110) [26].

Since surface alloying is a key mechanism to the formation of silicene by epitaxial growth on metal surfaces, this review will contain a description of surface alloying as relevant to the case at hand (Section 2). The experimental investigations of silicene on silver surfaces will be detailed in Section 3, while Section 4 will be devoted to the theoretical studies of silicene. Finally, our conclusions and future plans for silicene will be presented in Section 5.

2. Surface alloys: semiconductor on metal surfaces

Temperature dependence of metallic thin films deposited on metallic substrates has been the subject of many investigations in relation to possible technological applications. Indeed, the formation of surface alloys, which appear during the dissolution process of a thin film, can present new chemical and physical properties with regard to their small thickness (typically a few atomic layers). The composition of these surface alloys is closely related to both chemical interactions between elements (deposit and substrate) and a surface segregation tendency [27]; for a review, see for instance Refs. [28–30]. Most modern theories [31,32,28] describe the surface segregation phenomenon in metallic alloys as resulting from three main driving forces: (i) relative surface stress of pure elements; (ii) chemical interactions; and (iii) size mismatch. According to these models, the segregation phenomenon can in some cases appear as a precursor of the bulk phase transformations. Thus, surface segregation can lead to the formation at the surface of a pure plane of solute for systems showing a tendency to phase separation, and a two-dimensional ordered surface alloy for systems presenting a tendency to order. This has been experimentally observed for two model metallic systems: Ag/Cu(111) (phase separating system) [33,34] and