

## Density-Functional Theory Investigation of the Oxidation of Silicene on Graphitic Substrates

**Nazli Jodaeeas**<sup>1,2</sup>, Holger Vach<sup>2,3</sup> and Gilles H. Peslherbe<sup>2,4</sup>

<sup>1</sup>Department of Physics, Concordia University, Montreal, Canada

<sup>2</sup>Centre for Research in Molecular Modeling, Concordia University, Montreal, Canada

<sup>3</sup>CNRS-LPICM, Ecole Polytechnique, Université Paris-Saclay, Palaiseau, France

<sup>4</sup>Department of Chemistry and Biochemistry, Concordia University, Montreal, Canada

Silicene, a monolayer of silicon atoms, has received increasing attention due to its unique electronic and structural properties and potential applications in the electronics industry. Silicene typically produced on substrates such as silver has been shown to exhibit very high reactivity towards oxygen, which is a challenge for practical applications. Density-functional theory (DFT) calculations have indeed suggested that oxidation is a barrierless process for isolated silicene models (neglecting the role of the substrate). Only recently have low-buckled silicene nanosheets been synthesized on a nonmetallic and inert highly oriented pyrolytic graphite (HOPG) substrate, and in contrast to previous observations with other substrates, silicene on HOPG appears to remain stable with respect to oxidation after several weeks of air exposure. The stability towards oxidation of silicene/HOPG was hypothesized to be related to the low buckling of silicene on HOPG compared to that on metal substrates. Spin-polarized DFT calculations have been performed to investigate the interaction of the oxygen molecule and isolated low-buckled silicene, and in agreement with previous calculation results, the oxygen molecule dissociates and reacts with low-buckled silicene via an exothermic process without an energy barrier. Furthermore, a detailed analysis of the reaction mechanism reveals that electron transfer from silicene to the oxygen may be responsible for its barrierless dissociation and reaction with the support. To address the lack of reaction with oxygen of silicene on HOPG, DFT calculations are performed for the silicene oxidation pathway in the presence of the substrate. We will discuss our results, paying particular attention to possible electron transfer from silicene to the HOPG substrate (similar to that observed for antimonene on a graphene substrate), which could compete with electron transfer to the oxygen molecule along the reaction path and essentially prevent barrierless oxidation of silicene. This work underscores the importance of the subtle electronic effects that substrates may have on the reactivity/stability of the materials they are deposited on.