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Review article

# Two-dimensional silica opens new perspectives

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ABSTRACT

In recent years, silica films have emerged as a novel class of two-dimensional (2D) materials. Several groups succeeded in epitaxial growth of ultrathin $SiO_2$ layers using different growth methods and various substrates. The structures consist of tetrahedral [$SiO_4$] building blocks in two mirror symmetrical planes, connected via oxygen bridges. This arrangement is called a silica bilayer as it is the thinnest 2D arrangement with the stoichiometry $SiO_2$ known today. With all bonds saturated within the nano-sheet, the interaction with the substrate is based on van der Waals forces. Complex ring networks are observed, including hexagonal honeycomb lattices, point defects and domain boundaries, as well as amorphous domains. The network structures are highly tuneable through variation of the substrate, deposition parameters, cooling procedure, introducing dopants or intercalating small species.

The amorphous networks and structural defects were resolved with atomic resolution microscopy and modeled with density functional theory and molecular dynamics. Such data contribute to our understanding of the formation and characteristic motifs of glassy systems. Growth studies and doping with other chemical elements reveal ways to tune ring sizes and defects as well as chemical reactivities. The pristine films have been utilized as molecular sieves and for confining molecules in nanocatalysis. Post growth hydroxylation can be used to tweak the reactivity as well.

The electronic properties of silica bilayers are favourable for using silica as insulators in 2D material stacks. Due to the fully saturated atomic structure, the bilayer interacts weakly with the substrate and can be described as quasi-freestanding. Recently, a mm-scale film transfer under structure retention has been demonstrated. The chemical and mechanical stability of silica bilayers is very promising for technological applications in 2D heterostacks.

Due to the impact of this bilayer system for glass science, catalysis and the field of 2D materials, a large number of theoretical and experimental studies on silica bilayers have been reported in the last years. This review aims to provide an overview on the insights gained on this material and to point out opportunities for further discovery in various fields.



*Abbreviations*: 2D, two-dimensional; 3D, three-dimensional; AES, Auger electron spectroscopy; AFM, atomic force microscopy; DFT, density functional theory; EELS, electron energy loss spectroscopy; ESEM, environmental scanning electron microscopy; Gr, graphene; IRAS, infrared reflection absorption spectroscopy; LEED, low energy electron diffraction; LEEM, low energy electron microscopy; MD, molecular dynamics; ML, monolayer; ND, neutron diffraction; NMR, nuclear magnetic resonance spectroscopy; NP, nanoparticle; PMMA, poly(methyl methacrylate); SBU, secondary building unit; SPM, scanning probe microscopy; STM, scanning tunneling microscopy; STEM, scanning transmission electron microscopy; STS, scanning tunneling spectroscopy; TEM, transmission electron microscopy; TBPB, 1,3,5-tris(4-bromophenyl) benzene; UHV, ultra-high vacuum; UV–vis, ultraviolet–visible spectroscopy; XPEEM, X-ray photoemission electron microscopy; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction.

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**Contents**



## 1. Introduction

Silicon dioxide in its crystalline and glassy forms is of immense technological importance, with applications ranging from cladding skyscraper facades to manufacturing microchips. Knowledge and control of the structure are key for designing the right materials for each purpose. At the same time, silicates are abundant in nature, and understanding their structures is equally crucial for geology and plant science. Recently, a new class of ultrathin silica films was created, which allows unique insights and control over the atomic structure.

These films are typically grown 'bottom up', with building blocks deposited from the vapor phase, allowing finely tuned film thickness. Supported by metal substrates, their properties can be explored with various tools from surface science. This material class has garnered a great deal of attention over the last years, with publications reporting on structural, chemical and electronic properties employing a large number of techniques.

This review aims to summarize the current state of research on silica bilayer systems, and to point out gaps in the knowledge as well as future potential of this material class. A number of well-defined silica thin film structures have been presented at this point, all of them formed by tetrahedral [$SiO_4$] building blocks, as shown in Fig. 1a. Monolayers (ML) of these building blocks form highly ordered honeycomb lattices with the film stoichiometry $SiO_{2.5}$ [1], where three oxygen bridges are formed to neighboring tetrahedra, while the fourth oxygen bridge is connected to the substrate [2]. A side view schematic is shown in Fig. 1b. Since these films exhibit one covalent bond to the substrate per structural unit, their atomic structure is strongly directed by the substrate and it is not expected that monolayer silica films can exist without a support.

By adapting the preparation of silica thin films, it is possible to grow layers with two tetrahedral building units stacked on top of each other, connected by an oxygen bridge [3]. Since the remaining three oxygen bonds per structural unit are connected in-plane, this system exhibits no covalent bonds to the substrate, and also no dangling bonds, as shown in Fig. 1c. This film is frequently denoted as bilayer silica film or two-dimensional (2D) silica. In analogy to other 2D materials like graphene (Gr) and phosphorene, the 2D silica film has also been labelled as silicatene, although it does not possess any unsaturated

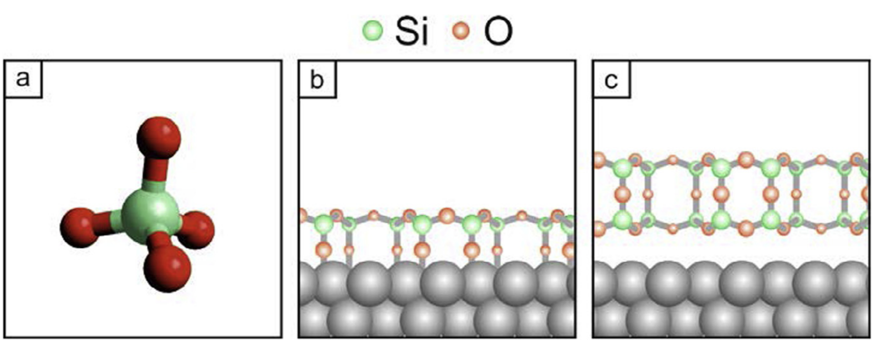


**Fig. 1.** Structure elements of silica layers. a) [$SiO_4$] tetrahedral building block. b) Side view of a monolayer film on a metal substrate. Tetrahedral building blocks are covalently bound to the substrate. c) Side view of bilayer film on a metal substrate. Tetrahedral building blocks of the top and the bottom layer are connected by perpendicular oxygen bridges in a mirror plane. The self-saturated oxide film interacts weakly with the substrate.

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