METANANO 2018 IOP Publishing
IOP Conf. Series: Journal of Physics: Conf. Series **1092** (2018) 012080 doi:10.1088/1742-6596/1092/1/012080

Surface Engineering of Two-Dimensional Hydrogenated Silicon Nanosheets for Tailored Applications

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Abstract. Approaching the predicted limits by Moor’s law, which come with the shrinking size of electronics, science needs to find alternatives for the fabrication of novel devices. Within the last decades, more and more hybrid materials have been developed based on 0D- 1D- and also 2D nanomaterials. This development is also driven by the search for fast, cheap, reproducible and environmental-friendly low-cost devices. Hydrogenated silicon nanosheets (SiNSs) consist of just a buckled monolayer of sp^3-hybridized silicon atoms, which are decorated with hydrogen atoms. The sheets show green and consistent photoluminescence at ~510 nm and are predicted show semiconducting behaviour. SiNSs may be used as an alternative for not only bulk silicon, but also already known two dimensional materials. Well-studied and established nanosilicon surface chemistry offers solid ground for precise surface engineering, leading to control of the nanomaterial for reproducible device fabrication. New applications and processing techniques can thus be developed, which lead to facile fabrication of enhanced sensors and (opto)electronics. In this regard, research pursues additionally the combination of organic materials’ properties with those of the nanomaterials, building the basis for new devices. One example is the combination of the widely used organic semiconductor poly(3-hexylthiophene-2,5-diyl) with the precisely modified SiNSs. Again, surface engineering plays the key role in the hybrid materials’ synthesis and subsequent application. This gives the opportunity to tune the properties of the hybrid material in the desired way. In this context, we present different ways of surface engineering with the modification of SiNSs as an example for the subsequent application in various (opto)electronic devices (*e.g.,* SGFETs and photonic sensors).

1. SiNSs as Novel Two-dimensional Material

With the discovery of graphene by Novoselov *et al.*, a new area of nano-based applied science has been discovered. Following this example, further two-dimensional (2D) analogues[1] such as *e.g.,* silicene, germanene[2], or transition metal dichalcogenides[3] have been synthesized and characterized.

The synthesis of silicene[4] and its hydrogenated form silicane[5][6] turned out to be particularly interesting, as silicon is the main element in the semiconductor industry. Starting with the chemical exfoliation of calcium ions from the crystalline $CaSi_2$ Zintl phase, nano-sized silicane, also referred to as layered polysilane, can be liberated. These slightly buckled free standing 2D silicon sheets (SiNSs), ranging from hundreds of nanometers to micrometers size, are nearly planar. With the small dimensions of SiNSs, new properties and possibilities arise, of which some examples are the green photoluminescence (PL) and the semiconducting behavior of the material. As already shown with the pioneer graphene, the band gap can be modified and Fermi level tuning can be performed *via* external influences on the surface.[7][8] This precise surface engineering of the nanomaterial can be either covalent or non-covalent. In the case of SiNSs, none of the methods leads to a significant deformation, or destruction of the surface, due to the sp^3-hybridized nature of the material. For covalent functionalization, the H atom is available on the surface, hence there is no need to introduce defects as with graphene. Physical strain[9], the underlying substrate[10], external electrical fields[11] and surface functionalization[12] are predicted to have an influence on physical properties of the nanomaterial and open the ability for the manipulation of the band gap. This approach can be used for surface engineering, leading to the tailored design of the surface, which is most suitable for the desired needs. Thus, new devices like SiNS-based photonic or humidity sensors can be fabricated. These could eventually replace the already widely used bulk silicon, which is limited by its features, such as the indirect energy band gap[13], lack of transparency and flexibility.

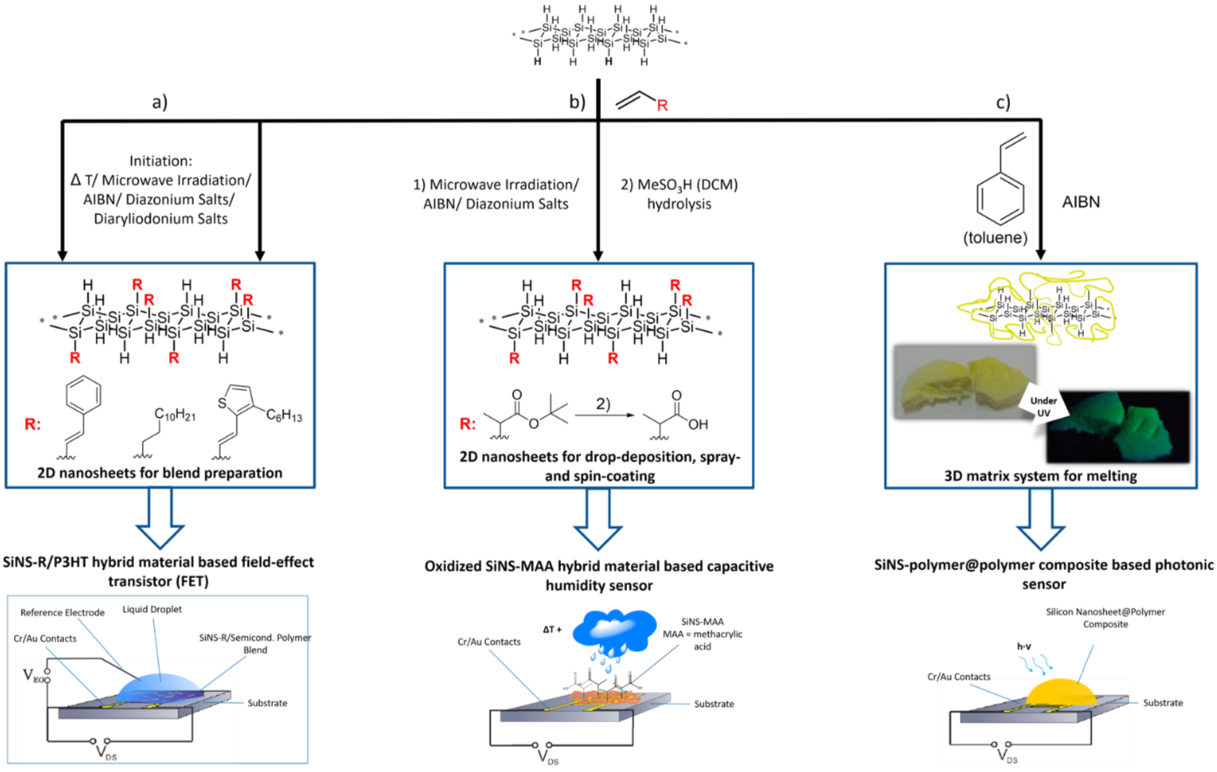

Figure 1: Surface engineering *via* functionalization of SiNSs using hydrosilylation on the surface of the Si-based 2D material. Different initiators can be used for the radical reaction, which lead to the functionalization with a variety of molecules. The modification introduces an additional property to the nanomaterial, such as additional π-electrons to the system (a), hydrophilicity of the surface (b) and encapsulation in a polymer (c). This step not only helps to protect the sensitive material from external influences, but also to control it for subsequent processing and application in novel nanomaterials-based electronics.

2. Surface Engineering of Nanomaterials

In general, to enable the use of these nanomaterials in ambient conditions and for facile big scale fabrication, they need to be controlled and stabilized.[14] Especially the 2D SiNSs tend to agglomerate right after their exfoliation, due to their high surface to volume ratio. Additionally, like most of the silicon-based materials, they show high affinity to oxygen and can therefore be destroyed by high energy light (UV light) and reaction with air-oxygen.[15] As a result, the formation of silicon dioxide takes place, which is an insulator with a wide energy band gap[16]. SiNSs can be stabilized *via* adjusted surface functionalization, which was already described in our previous works.[15][17] A variety of organic functional groups, such as dodecene, styrene or *tert*-butylmethacrylate (^{t}BMA) were attached to the surface, using thermal energy, diazonium salts[15], or AIBN[17] as an initiator for a hydrosilylation reaction. This surface modification is a significant increase in the lifetime of SiNSs. Additionally, the nanomaterial can be controlled more easily, due to the possibility to prepare various dispersions, which can be used for subsequent device fabrication. Different material deposition techniques, such as spray deposition or spin coating can be applied. As a result, reproducible and ultra-low-cost conductive patterns *via* inkjet printing technique[18] can be possible in the future, which is currently under further investigation in our group.

Hydrosilylation reaction and simultaneous radical polymerization has also been used for the synthesis of a composite SiNSs-polymer@polymer, which consists of functionalized and at the same time in a polymer matrix embedded SiNSs. This three-dimensional network is formed in a one-step reaction, offering both materials' properties. Thus, the features of the polymer open up even more new possibilities for application. As we could already show in our previously published work[19], new photosensitive devices can be built based on these composites. As an example, polystyrene has been used to embed and functionalize SiNSs, forming SiNS-PS@PS. The resulting composite can be melted on top of pre-patterned gold electrodes, forming an optoelectronic sensor. In this case, both rigid and flexible substrates can be used. Very sensitive optical response can be detected using this device, while exposing it to a light source with wavelengths lower than 450 nm.

Combining the high surface to volume ratio and the surface engineering of SiNSs with functional groups, we went further and realized the fabrication of the first oxidized SiNSs (OSiNSs)-based capacitive humidity sensors. First, ^{t}BMA was used as functional molecule for the modification of the SiNSs' surface. The *tert*-butylic ester group of the methacrylic acid can be *e.g.,* exposed to saponification.[20] This lead to the formation of methacrylic acid groups (MAA), covering the surface of the SiNSs and thus resulted in a facile transformation of the properties of the hybrid material. These hydrolysis reactions only take place with the functional groups of the organic molecules on the SiNSs' surface. Thus, the Si-Si-bond splitting can be excluded. The hydrophilic nature of the herewith synthesized hybrid material is crucial for the device to be able to work as a humidity sensor. In an additional step, the hybrid material was oxidized, in order to form highly porous OSiNS-MAA structure, which can be penetrated by surrounding water molecules. These can interact with the hybrid material and influence its dielectric behavior, resulting in a change in the capacitance. For the measurements, the humidity at a constant temperature was changed from around 25% relative humidity (RH) to up to 95 %RH. In general, this modification method shows an additional way for properties tuning of the hybrid material. A variety of further applications without destroying the conductive core can be developed.

In this work, not only an established way for a facile synthesis of hybrid materials, such as functionalized SiNSs and SiNS-based polymer composites, is highlighted, but also a detailed characterization of the surface with a variety of analysis techniques is presented. Furthermore, first steps towards optoelectronic applications are described. A facile integration of the modified and in a polymer matrix embedded SiNSs into the already well-known fabrication methods and the first prototypes of a highly sensitive photonic sensor are presented. Additionally, the successful fabrication of a SiNSs-based humidity sensor is described. This enables new possibilities in the field of capacitive sensors, whereby the first steps towards response to surrounding molecules, such as water at a certain temperature, are studied.

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