Room-temperature synthesis of earth-abundant semiconductor ZnSiN$_2$ on amorphous carbon

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This manuscript reports room-temperature one-step synthesis of earth-abundant semiconductor ZnSiN$_2$ on amorphous carbon substrates using radio frequency reactive magnetron co-sputtering. Transmission Electron Microscopy and Rutherford Backscattering Spectrometry analysis demonstrated that the synthesis has occurred as ZnSiN$_2$ nanocrystals in the orthorhombic phase, uniformly distributed on amorphous carbon. The technique of large-area deposition on an amorphous substrate can be interesting for flexible electronics technologies. Our results open possibilities for environmentally friendly semiconductor devices, leading to the development of greener technologies.

Results and discussion

In Fig. 1a, we present an ADF-STEM (Annular Dark Field-Scanning Transmission Electron Microscopy) micrograph, where it is possible to observe a bright contrast corresponding to the region with the synthesized compound. This contrast comes from the nanostructures examined, which appear as bright small dots. We would like to emphasize that ADF-STEM mode was intentionally applied to maximize contrast-diffraction effects, which is possible because those nanostructures have a clear crystalline character. It is possible to observe that the bright
dots are evenly distributed on the amorphous carbon area. Finally, a set of EDS (Energy Dispersive X-rays Spectroscopy) maps of ZnSiN₂ demonstrates the uniform distribution of nanostructures on amorphous carbon, in corroboration with the ADF-STEM micrograph. Figure 1b shows a SAED (Selected Area Electron Diffraction) pattern of ZnSiN₂ with an annular pattern originated from nanocrystals and the amorphous substrate. Those rings are highlighted with a violet semicircle with the corresponding ZnSiN₂ family of planes indexed as (120), (002), and (230) of the orthorhombic phase, according to theoretical calculations for this material²⁷.

In Fig. 2 we detail the nanostructures presented in Fig. 1 using high magnifications. Figure 2a presents an ABF-STEM (Annular Bright Field-Scanning Transmission Electron Microscopy) micrograph showing the distribution and morphology of ZnSiN₂ nanostructures. The bright small dots viewed in Fig. 1a now can be seen as dark dots and demonstrate the uniform distribution of the nanostructures on amorphous carbon, reinforcing the synthesis capability by using sputtering deposition. Besides, the nanostructure sizes are practically uniform, indicating the potential for nucleation since the initial synthesis at room-temperature. This characteristic can be useful, for example, in 2D materials synthesis aiming photocatalyst applications as done in the work from Bai et al.⁴³. In this study, the authors explain that ZnSiN₂ can have a higher band gap with respect to other zinc

Figure 1. (a) ADF-STEM image and a set of EDS maps of a region with deposited ZnSiN₂, showing the presence of Zn (green), Si (yellow) and N (blue). (b) SAED pattern with the correspondent diffraction planes.
nitrides (like ZnGeN2 and ZnSnN2), being proposed as efficient photocatalysts for water splitting. According to the first perspective, we believe that our work opens the possibility of manufacturing devices like thin film transistor (TFT) due to the potential production of single layers with a wide band gap in a large-scale/large-area with good uniformity.

Figure 2b shows the HAADF-STEM (High-Angle Annular Dark Field) image of ZnSiN2 in corroboration to Fig. 1a. Here we aim to explore variations in atomic number from elements in the sample. In this micrograph, it is possible to observe that the nanocrystals are displayed in higher contrast, because of the reduction of the contribution from amorphous carbon in the image formation. The nanocrystals observed in Fig. 1a are in agreement with HAADF measurement in Fig. 2b which show that ZnSiN2 synthesis has occurred effectively. In Fig. 2c is possible to observe the interplanar spacing of ZnSiN2 nanostructures distributed on amorphous carbon. This HRTEM (High-Resolution Transmission Electron Microscopy) micrograph was obtained in the region between ZnSiN2/amorphous-carbon and the void, displaying the interplanar spacing that matches the crystallographic planes of the orthorhombic phase of ZnSiN2 also in accordance with Fig. 1b.

In addition to TEM measurements, we present our quantitative analysis using RBS (Rutherford Backscattering Spectrometry). Figure 3 shows the RBS spectrum of ZnSiN2 and its RBS simulation performed by the RUMP code. The RBS measurement was obtained from ZnSiN2 synthesized on SiO2/Si (see Fig. 4b) complementing the qualitative EDS analysis (Fig. 1). It is possible to observe that the edge from Zn, Si, and N signals are well defined in the RBS spectrum of Fig. 3, which corroborates the presence of those elements in our synthesized material. The signals from the backscattered “He” from Zn appear at around channel 344 while from Si is pronounced like a single edge around channel 242 and from N is smoothly delineated around channel 142. The RBS signal
around channel 156 is originated from oxygen in the SiO2/Si substrate. We use a layered structure in order to effectively simulate the experimental spectrum of ZnSiN2: layer 1: 7 nm of ZnSiN2 layer composition; layer 2: 25 nm of SiO2; layer 3: silicon substrate. This layered model is suitable to simulate the Zn and Si signals in the RBS spectrum, indicating the good quality of our fit. Once the sputtering technique promotes a uniform synthesis of the ZnSiN2 on amorphous carbon (as demonstrated in Fig. 1), it is reasonable to expect that the synthesized ZnSiN2 is also evenly distributed on SiO2/Si. Therefore, we have demonstrated that our synthesis was successfully also in both, large-area amorphous carbon and large-area silicon oxide. It is important to point out that this work shows that we were able to promote a large-area of material synthesis through a single-step technique at room temperature, features that can be of interest for TFT technologies. In this context, it is important to notice that the manufacturing of flexible TFT at room temperature using amorphous oxide semiconductors is already a reality. In reference the authors expressed the importance of TFT fabrication at room temperature, as well as the production in large-area for the development of flexible electronic devices. Furthermore, flexible and freestanding single layers zinc-based semiconductors, produced in large areas have been promising to enhance solar water-splitting efficiency, as well as for other photovoltaic applications.

Conclusion
In summary, we report room temperature one-step synthesis of earth-abundant and non-toxic semiconductor ZnSiN2 on amorphous carbon substrates by using radio frequency reactive magnetron co-sputtering. The synthesis occurred as nanocrystals of ZnSiN2 in its orthorhombic phase. The synthesis technique demonstrates to be capable to produce ZnSiN2 in large-scale/large-area on amorphous substrates while taking into account greener concepts applied to advanced materials for flexible electronics.

Experimental section
Synthesis. ZnSiN2 was synthesized by sputtering using Zn and Si targets (both with 99.99% purity) simultaneously under a mixed Ar (50 sccm) and N2 (10 sccm) atmosphere for a nominal chamber pressure of 5 mTorr. The system base pressure was 1 × 10−7 Torr. Figure 4a shows the schematic setup of the synthesis chamber, where Zn and Si targets were kept under RF power of 51 W and 109 W, respectively. A Ni holey carbon grid (Quantifoil Q25035 R2/1 200 M) usually applied in TEM experiments was fixed on a SiO2/silicon substrate maintained at room temperature and in constant rotation during the synthesis. Figure 4b shows the grid/substrate accommodated on the holder, highlighting the grid (~ 3 mm diameter) separately, showing the morphology of the carbon amorphous region where the ZnSiN2 synthesis will be held. Before synthesis, the silicon substrate was cleaned with acetone, isopropyl alcohol, and deionized water. The carbon grid was used for TEM experiments. The material deposited on SiO2/Si was submitted to RBS measurement.

Characterization. A JEOL FEG JEM 2100F transmission electron microscope (TEM) operated at 200-kV of acceleration voltage and equipped with an energy-dispersive x-ray spectrometer (EDS-Noran Seven) was used for HRTEM, SAED, and EDS maps. The STEM mode images were obtained using an annular dark-field (ADF) and annular bright-field (ABF) detectors. EDS measurements were performed in STEM mode. RBS was employed to evaluate the overall composition of the synthesized sample. It was carried out by using a 1.2-MeV 4He++ ion beam produced by the 3-MV Tandetron accelerator from High Voltage Engineering Europa of the Ion Implantation Laboratory at Universidade Federal do Rio Grande do Sul (UFRGS), Brazil.
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Author contributions
H.C.-J. conceived the idea of this work and wrote the manuscript. H.C.-J., R.P.L., and B.G.S performed the sputtering synthesis. H.C.-J. and C.L. performed the TEM characterization. H.C.-J. performed the RBS analysis. R. L. S. organized and supervised the work. All authors discussed the results and revised the manuscript to the final format.

Competing interests
The authors declare no competing interests.

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