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Fabrication and Characterization of Fe-Doped SnSe Flakes Using Chemical Vapor Deposition

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Abstract: The development of two-dimensional (2D) materials has gained significant attention due to their unique properties and potential applications in advanced electronics. This study investigates the fabrication and characterization of Fe-doped SnSe semiconductors using an optimized chemical vapor deposition (CVD) method. Fe doping was achieved by dissolving FeCl₃ in deionized water, applying it to SnSe powder, and conducting vacuum drying followed by high-temperature CVD at 820 °C. Structural and morphological properties were characterized using optical microscopy, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). Results revealed differently shaped flakes, including rectangles, discs and wires, influenced by Fe content. Micro-Raman spectroscopy showed significant vibrational mode shifts, indicating structural changes. X-ray photoelectron spectroscopy (XPS) confirmed the presence of Sn-Se and Fe-Se bonds. Electrical characterization of the memristive devices showed stable switching between high- and low-resistance states, with a threshold voltage of 1.6 V. These findings suggest that Fe-doped SnSe is a promising material for non-volatile memory and neuromorphic computing applications.

Keywords: Fe-doped SnSe; chemical vapor deposition; memristive devices



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1. Introduction

The exploration of two-dimensional (2D) materials has gained significant attention in recent years due to their unique physical properties and potential applications in next-generation electronic devices. Group IV monochalcogenides, such as SnSe, SnS, GeSe, and GeS, have been shown to exhibit promising characteristics, making them viable alternatives to the more commonly studied transition metal dichalcogenides (TMDCs) [1]. These four materials possess a corrugated, highly anisotropic structure, exhibit a non-zero bandgap, and undergo additional symmetry breaking, due to the uneven occupation of atomic sites. These inherent properties, combined with their earth abundance and low toxicity, have made them attractive candidates for a wide range of applications over the past few decades. Examples of such applications include thermoelectrics [2], ion batteries [3], optoelectronics [4], photodetectors [5], and photovoltaic devices [6].

Among these, SnSe, a p-type semiconductor, possesses an orthorhombic crystal structure in space group Pnma (62) with atoms arranged in two adjacent double layers of tin and selenium held together by weak van der Waals interactions [7]. This structure grants SnSe a narrow band gap (1.3 eV direct and 0.9 eV indirect) [8], making it suitable for a wide range of applications such as memory switching devices [9], photovoltaic devices [10], and optoelectronic devices [11]. The ability of SnSe to be reduced to bi-/monolayer forms due to its van der Waals structure enhances its potential for miniaturized and nanoscale semiconducting applications [12]. For instance, SnSe-based memristors have shown lower power consumption compared to other similar devices [9], while SnSe-based photodetectors offer high responsivity and fast response times [13]. Additionally, the material's potential as an

electrode material in energy storage devices further extends its applicability in modern technology [14]. These attributes highlight the broad applicability of 2D SnSe, making it a valuable material for next-generation electronic devices.

Various strategies have been used to synthesize SnSe, including thermodynamic and kinetic-control approaches. Physical vapor transport (PVT) is a thermodynamic process recently found to produce high-quality 2D crystals with more stable atomic structures, suggesting its potential as an important technique for obtaining 2D materials for optoelectronics applications [15]. During the PVT process, SnSe powder evaporates under controlled thermodynamic conditions and recrystallizes on the cold surface of a substrate, forming nanoflakes with uniform thickness and excellent crystallinity [16].

Doping SnSe with transition metals (TMs), can further enhance its properties by introducing new functionalities, such as magnetic behavior, which are important for advanced electronic applications [17,18]. Memristive devices, which exhibit a memory-dependent resistance, are particularly interesting for their potential use in non-volatile memory and neuromorphic computing systems [19,20]. These devices require materials that can reliably switch between high- and low-resistance states. TM-doped SnSe, as a diluted magnetic semiconductor, offers a promising route to achieving stable and controllable memristive behavior.

Previous computational studies on doping group IV monochalcogenides have primarily focused on elements like Cr, V, and Co [21]. Research on Cr-doped SnSe has shown that it maintains a ferromagnetic ground state, with each Cr atom introducing a magnetic moment of 4 μ_B . However, Cr-doped SnSe is a half-metallic semiconductor, exhibiting metallic properties in one spin channel and a band gap in the other. V-doped SnSe, while maintaining ferromagnetism, exhibits a smaller band gap of about 0.10 eV, which can limit its application range as a magnetic semiconductor. Co-doped SnSe also exhibits a ferromagnetic ground state but with a negligible band gap, sometimes considered almost half-metallic. Recent research on Bi-doped SnSe memristors has demonstrated the potential of such devices for neuromorphic computing applications, particularly in enhancing ferroelectric properties and achieving high linearity in long-term potentiation and depression (LTP/LTD) behaviors [22].

Fe doping is another viable path forward. During the doping process, Fe atoms substitute for Sn atoms within the SnSe lattice, introducing localized magnetic moments due to the unpaired electrons of the Fe atoms. This substitution can slightly distort the crystal structure, affecting both the electronic band structure and magnetic properties of the material. Such modifications can lead to new electronic states and alter the charge carrier concentration and mobility, significantly impacting the material's electrical and magnetic properties. Despite the promising characteristics of Fe-doped SnSe, experimental studies on this topic are limited, highlighting the need for further investigation.

In this study, our primary goal is to explore the effects of Fe doping on the structural and morphological properties of SnSe flakes. While our focus is on obtaining and characterizing Fe-doped SnSe flakes using a novel chemical vapor deposition technique, we also present preliminary results on their integration into memristive devices, highlighting the potential applications of these doped materials.

2. Materials and Methods

To fabricate 2D semiconductors doped with transition metals, we utilized the optimized CVD method depicted in Figure 1a. The method was initially developed for obtaining monocrystalline monochalcogenide SnSe flakes on silicon substrates with a surface layer of SiO₂ (300 nm in thickness) [9].

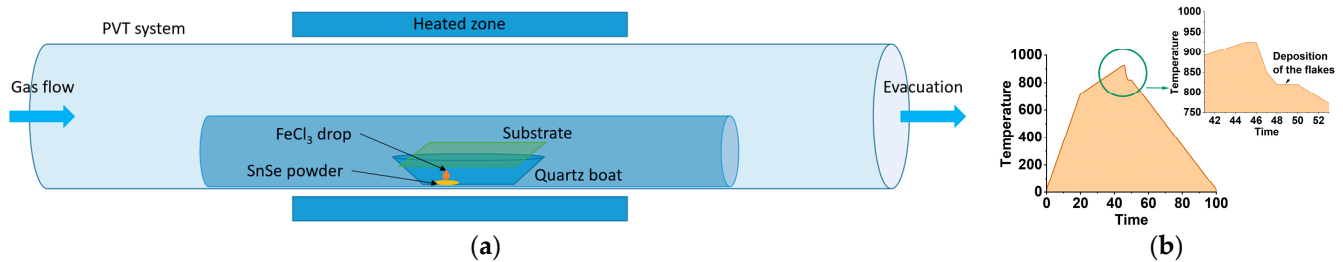


Figure 1. Synthesis recipe. (a) Schematic representation of the PVT system used for the synthesis of Fe-doped SnSe flakes, (b) the programmed furnace temperature during the entire process.

The optimized preparation recipe, which ensures the synthesis of Fe-doped SnSe flakes with controlled thickness and lateral size, involves the following key aspects.

In order to obtain Fe-doped SnSe flakes as thin as possible (2D flakes), the CVD deposition must be assisted by an inert gas flow to ensure a small angle of incidence of the vapors on the deposition substrate. Thus, in the deposition chamber with inert atmosphere, a downstream and upstream area can be defined.

To achieve Fe doping levels in SnSe compatible with dilute magnetic semiconductors, the hygroscopic FeCl₃ (99.99% purity) powder must be accurately weighed in the CVD experiments. Therefore, it was dissolved in deionized water (at a concentration of 2 mg FeCl₃/mL) and its solution was dropped onto SnSe powder placed in the upstream of a quartz boat. Since FeCl₃ boils at 316 °C and the deposition temperature for SnSe is much higher (820 °C), we used increasing amounts of FeCl₃, as presented in Table 1.

Table 1. Source material quantities used in vapor deposition experiments.

Composition No.	SnSe (mg)	FeCl ₃ (mg/mL)	Theoretical Composition
1	2.3	0.4/0.2	(Sn _{0.83} Fe _{0.17})Se
2	3.9	0.8/0.4	(Sn _{0.80} Fe _{0.20})Se
3	1.4	0.4/0.2	(Sn _{0.74} Fe _{0.26})Se

To optimize the deposition process, the SiO₂ (300 nm)/Si substrate is placed on the quartz boat at a precise distance of 5 mm from the SnSe and FeCl₃ powders. The length of the substrate is carefully selected to cover a significant portion of the quartz boat, ensuring maximum interaction with the vapor phase. The substrate is positioned with a 3 mm gap between its upstream edge and the edge of the boat, allowing the inert gas flow to pass underneath. A similar gap is maintained at the downstream edge for the exit of the gas flow. This configuration promotes a higher partial pressure of the vapors and enhances the vapor transport phenomena, essential for the efficient deposition of Fe-doped SnSe flakes.

The quartz boat is placed in a quartz tube with a diameter of 2.54 mm and a length of 800 mm. The quartz tube is then inserted into a PVT deposition system consisting of a tubular furnace and a quartz tube with a diameter of 50 mm and a length of 1800 mm with closed ends. Specifically, the quartz tube is introduced so that the upstream edge of the quartz boat was 6 mm from the downstream edge of the heated zone of the furnace. The furnace lid is closed tightly, and the 50 mm quartz tube is sealed and evacuated to 1×10^{-5} bar, followed by purging with 5N-purity nitrogen at 1.1 bar pressure. This vacuum purging sequence is repeated three times, to ensure negligible oxygen residue in the quartz tube. At the same time, during this process, the water in which the FeCl₃ powder was dissolved is evaporated.

The furnace is heated following the program presented in Figure 1b. The deposition of Fe-doped SnSe flakes is conducted at a precise temperature of 820 °C for a duration of 2 min, with a nitrogen flow rate of 100 sccm. To achieve this controlled heat treatment, the furnace is initially brought to a higher temperature of 925 °C. Subsequently, it is repositioned so that the quartz boat, which was initially located outside, near the heated zone, is moved

into the center of the heated area. The higher initial temperature allows the surplus thermal energy to be utilized for the rapid heating of the tube and the quartz boat, ensuring that the temperature stabilizes at the desired 820 °C after one minute. Throughout all preliminary phases, continuous nitrogen purging is maintained to ensure that the deposition occurs precisely at the target temperature.

The furnace was then turned off and purged with nitrogen. It was moved 80 cm away, so that the quartz boat is outside the downstream edge of the furnace. A higher nitrogen flow rate is used to eliminate residual vapors and facilitate rapid cooling of the silicon substrate.

Optical microscopy images were captured using an OPTIKA microscope (Budapest, Hungary) with magnifications ranging from 50× to 800×. This microscope was equipped with a trinocular head, halogen lighting, and a polarizing kit.

For morphological and elemental characterization, we employed a Zeiss Gemini 500 scanning electron microscope (SEM, Zeiss, Oberkochen, Germany) equipped with an energy dispersive X-ray (EDX) spectrometer from Bruker (Billerica, MA, USA).

Micro-Raman spectra were recorded in backscattering geometry using a LabRAM HR Evolution Raman spectrometer from HORIBA Jobin-Yvon (Palaiseau, France). This spectrometer was equipped with a confocal microscope and a helium–neon (He-Ne) laser operating at an excitation wavelength of 633 nm. The laser radiation was focused on the sample surface using an Olympus 100× objective (Tokyo, Japan). To prevent heating effects, the laser power was maintained at a suitably low level. The Raman-shift calibration was performed using the Si peak at 520 cm^{−1}.

The XPS studies were conducted with a SPECS XPS spectrometer (SPECS Surface Nano Analysis GmbH, Berlin, Germany). The monochromatized X-ray source (Al K α line, energy 1486.7 eV) was operated at 20 mA and 12.5 kV (250 W). Charge compensation was achieved using a neutralizer operated at 0.5 V $\times$ 0.1 mA and calibration with respect to the C=C contamination line at 284.6 eV. The pressure during the measurement was maintained at 10^{−9} mbar.

Memristive devices were fabricated using the Fe-doped SnSe flakes. The process began with the preparation of the substrate. Silicon wafers with a 300 nm thick SiO₂ layer were cleaned by sequential washing with acetone and isopropanol, followed by drying with a nitrogen pistol. A thin adhesion layer of TI PRIME was applied using a spin coater (Spin Coater Cee®2008), followed by the deposition of the photoresist (AZ 5214E) through the same method. To ensure proper adhesion and resolution during UV exposure, the substrates underwent thermal treatment to remove residual solvents. The photolithography process involved UV irradiation using an EVG 620 Mask Alignment System in a cleanroom environment (class 100, ISO EN 14644). The exposure was conducted in two stages: initial low-power exposure with the patterned mask, followed by a thermal treatment, and a second exposure with a blank mask. The exposed areas were then developed in an AZ 726 MIF developer. Thin metal films were deposited in two steps: a 10 nm titanium adhesion layer was applied by magnetron sputtering, followed by the deposition of a 200 nm gold layer using thermal evaporation (Tectra GmbH Physikalische Instrumente equipment). After deposition, the samples were immersed in acetone to remove the remaining photoresist and lift off excess metal, leaving behind well-defined Au/Ti contacts.

For the transfer process, Fe-doped SnSe flakes were dry-transferred onto the fabricated contacts. The desired flakes were located on the Si/SiO₂ growth substrate using an optical microscope. A small piece of PDMS was then cut, steamed using a hot plate set at 120 °C, and placed on the substrate where the selected flakes were positioned. The PDMS, now carrying the flakes, was gently lifted and positioned over the Au/Ti contacts under the microscope, ensuring precise alignment. The PDMS was then softly removed, leaving the flake accurately placed on the contacts.

The devices were electrically characterized by recording the direct current (DC) current–voltage (I–V) sweeps. Electrical measurements were performed using a Keithley 4200A-SCS Parameter Analyzer (Solon, OH, USA).

3. Results

3.1. Optical Microscopy

Using optical microscopy, we observed the formation of various shapes, stripes, and wires of Fe-doped SnSe (Fe:SnSe) on the surface of SiO₂/Si substrates, depending on the three different compositions of the source materials (as shown in Figures 2–4).

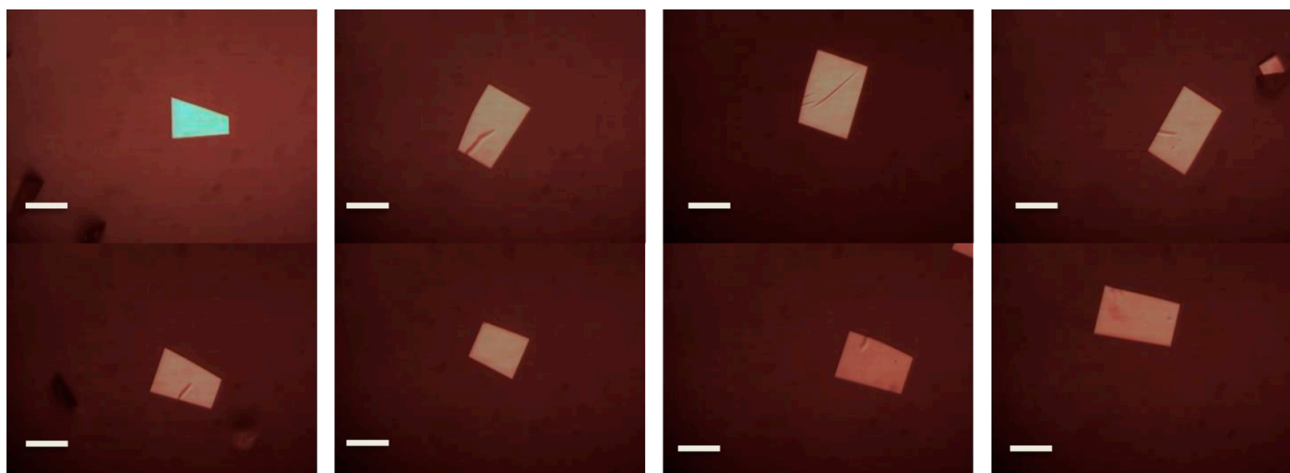


Figure 2. Optical images of Fe-doped SnSe flakes (800× magnification) of rectangular shapes and different sizes obtained using the source materials with composition no. 1. The scale bar in each image is 20 μm.

The shape of Fe:SnSe flakes obtained for composition no. 1 of the source materials (Figure 2) were the closest to those for undoped SnSe [9]. These flakes exhibited an average lateral size of approximately 25 μm (size distribution is given in Figure 5), with thicknesses varying, including some flakes having a thickness below 150 nm. Figure 2 presents a selection of these flakes. As can be observed, the flakes predominantly exhibit a rectangular shape, which is characteristic of the orthorhombic structure of the SnSe phase [23,24]. The uniform contrast in the optical microscopy images suggests that the flakes have a consistent thickness across their lateral dimensions.

Additionally, some folded flakes are visible in the images. The presence of these folded flakes can be attributed to the mechanical properties of the 2D SnSe layers. Due to their thin nature, these flakes are flexible and can fold over upon themselves during the growth process, due to interactions with the substrate. This folding behavior is a common occurrence in 2D materials, reflecting their high aspect ratio and the weak van der Waals forces holding the layers together, which allow for bending and folding without fracturing [25].

Starting with composition no. 2 of the source materials (Figure 3), the number of objects with shapes different from those specific to undoped SnSe began to increase significantly. We observed the formation of stripes, which grew one on top of one another in a layered manner, resembling walls (Figure 3a). The size of the flakes decreases, as compared to the previous composition, to 20 μm (Figure 5). More importantly, there was the formation of wires that originated from grains on the substrate surface. These wires exhibited a remarkable range of lengths, varying from a few micrometers to tens of micrometers or even over one hundred micrometers. The growth orientation of these wires varied; some grew obliquely above the substrate (Figure 3b,c), while others grew almost vertically (Figure 3d). The wires are indicated with yellow ellipses in the figures.

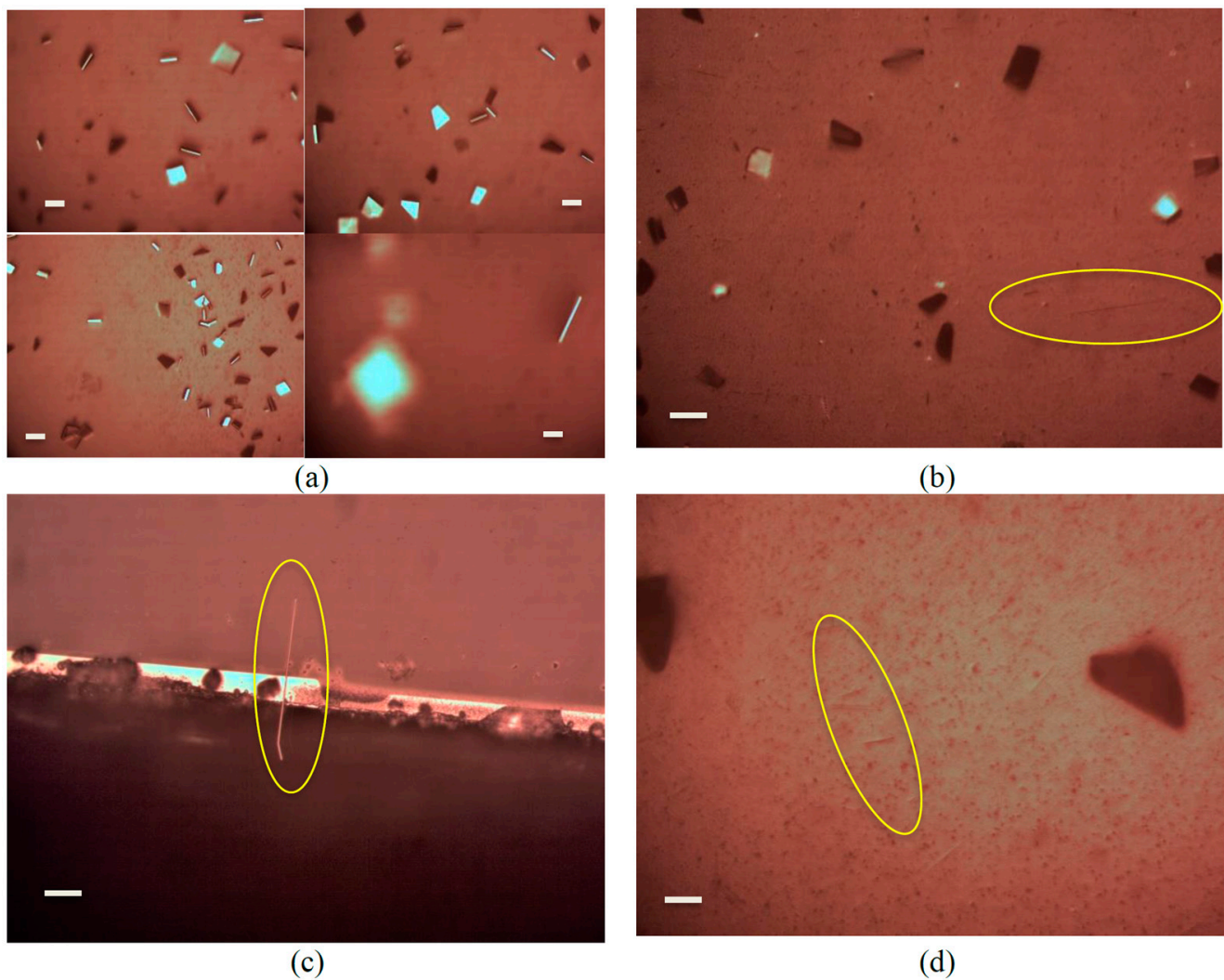


Figure 3. Optical images of Fe-doped SnSe objects ($400\times$ magnification) of different shapes and sizes formed using source materials with composition no. 2. Different shaped-flakes such as rectangles, stripes and wires are shown in (a–d). The scale bar in each image is $20\text{ }\mu\text{m}$.

The introduction of Fe doping into SnSe can significantly alter the growth dynamics and morphology of the resulting structures. The presence of Fe atoms in the SnSe matrix changes the regular lattice structure, leading to increased nucleation sites and altered growth kinetics. As the Fe content increases, these changes become more pronounced, resulting in the formation of non-standard shapes and structures. The formation of stripes and wires, rather than the typical rectangular flakes observed in undoped SnSe, indicates that Fe doping introduces significant modifications to the crystal growth process.

The stripes that form one on top of one another like walls could be attributed to the anisotropic growth tendencies induced by Fe doping. The Fe atoms may preferentially segregate to specific crystallographic planes, promoting directional growth along these planes. This directional growth can lead to the formation of layered structures, as observed in the stripes. The wall-like appearance suggests a step-growth mechanism where new layers form on top of existing ones, driven by the localized concentration of Fe.

The formation of wires growing from grains on the substrate surface can be explained by the catalytic role of Fe in promoting one-dimensional growth. Fe atoms can act as catalysts, facilitating the formation of wire-like structures through a vapor–liquid–solid (VLS) growth mechanism [26]. In this process, Fe atoms assist in the adsorption and diffusion of Sn and Se atoms on the substrate surface, leading to the nucleation and elongation of wires. The varying

orientations of the wires—oblique or vertical—can be influenced by the local concentration of Fe, the substrate surface properties, and the growth conditions.

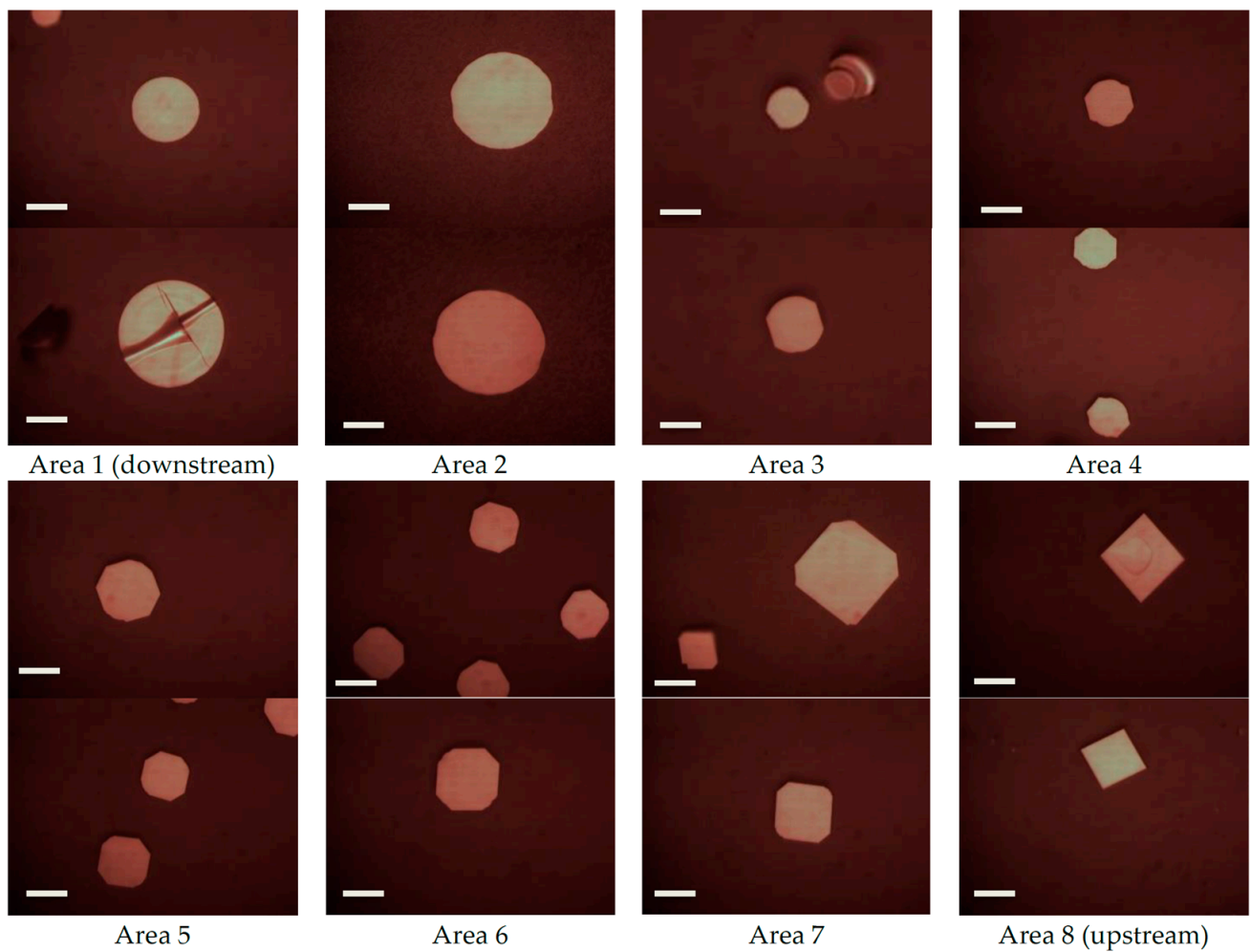


Figure 4. Optical images of Fe-doped SnSe flakes ($800\times$ magnification) of different shapes and sizes formed using source material with composition no. 3. The scale bar in each image is $20\text{ }\mu\text{m}$.

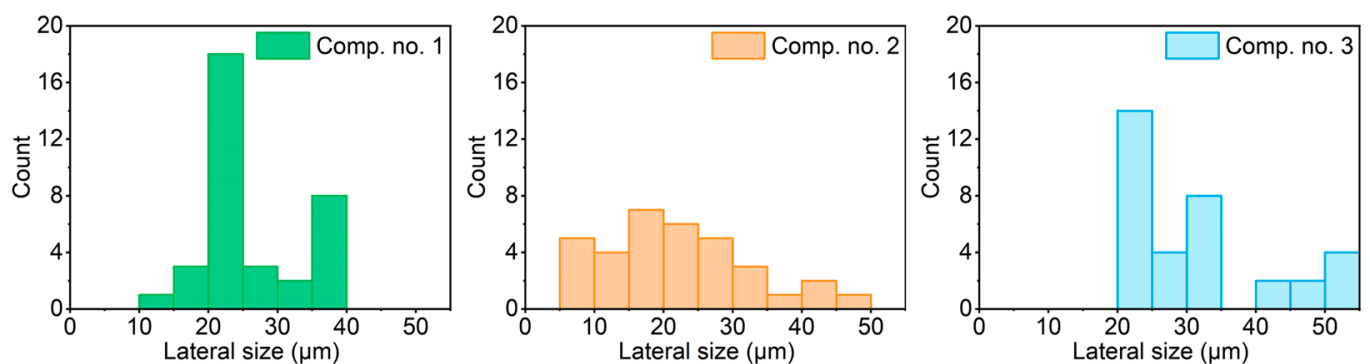


Figure 5. Lateral size distribution of Fe-doped SnSe flakes obtained from compositions no. 1, no. 2, and no. 3. The histogram shows the count of flakes within specific lateral size ranges for each composition.

The VLS mechanism is a well-established method for the synthesis of one-dimensional nanostructures. In the presence of a catalyst, the vapor-phase precursors condense into a liquid droplet, from which the solid phase grows in a controlled manner. Fe atoms, serving

as the catalyst, enable the VLS process by lowering the energy barriers for nucleation and growth, resulting in the formation of elongated wire-like structures [27].

The increased Fe content enhances the likelihood of wire formation by providing more catalytic sites for VLS growth. Additionally, the wires' considerable length, ranging from a few micrometers to over one hundred micrometers, indicates that Fe doping not only promotes nucleation but also sustains wire growth over extended periods. The presence of Fe modifies the chemical potential and diffusion barriers, allowing for continuous elongation of the wires.

The Fe:SnSe flakes obtained for composition no. 3 of the source materials were remarkable (Figure 4), showing a gradual transition of their shape from rectangular to circular as we moved from the upstream edge of the substrate towards its downstream edge (Figure 4). Despite having the same experimental conditions as for the previous two compositions (the source materials, SnSe and FeCl₃, are concentrated towards the upstream edge), the increased Fe content in composition no. 3 introduces distinct growth dynamics. The shape of the flakes was specific to a certain area of the substrate, between the upstream and downstream edges, as shown in Figure 4. The increased Fe content creates more localized nucleation sites. At the upstream edge, where the Fe concentration is lowest due to nitrogen flow, these sites promote the formation of well-defined rectangular flakes due to the lower nucleation rate. As the Fe concentration increases towards the downstream edge, the increased number of nucleation sites allows for larger, more isotropic growth, resulting in circular flakes. These observations indicate that a high doping level and distribution of Fe in SnSe significantly influence the morphology and growth patterns of the deposited microstructures. The size of the flakes is, on average, 25 µm, with larger flakes at the edges of the substrate (Figure 5).

The distribution for composition no. 1 shows a predominance of flakes with lateral sizes around 25 µm, indicating that this composition yields the most regularly shaped and consistently sized flakes. In contrast, composition no. 2 exhibits a wider range of smaller flake sizes, with a notable peak around 20 µm. This suggests that the increased Fe content in composition no. 2 leads to more varied nucleation sites and smaller-flake formation. Composition no. 3 displays an even broader size distribution, with flakes ranging from around 20 µm to 50 µm, indicating significant morphological changes induced by the highest Fe content. The presence of larger flakes in composition no. 3 suggests that higher Fe content promotes more extensive growth, resulting in larger structures.

To address the reproducibility and control over the morphology of Fe-doped SnSe flakes, we conducted extensive experiments across different compositions. The morphologies obtained using source materials with composition no. 1 and 2 were consistently reproduced across multiple trials, demonstrating the reliability of our synthesis process. These compositions reliably yielded well-defined rectangular flakes and other 2D structures with slightly varied shapes. For source materials with composition no. 3, the observed morphology was not stochastic, but rather exhibited a systematic, monotonic variation across the substrate. Specifically, we observed a transition from rectangular flakes in the upstream region to circular flakes in the downstream region. Each distinct morphology consistently formed in specific regions of the substrate, with no random mixing, indicating a controlled synthesis process driven by the specific conditions used.

3.2. SEM/EDX Measurements

Using SEM and EDX, we investigated the morphology and elemental composition of the disc-shaped flakes presented in Figure 4. We focused on these flakes because their shape is the most different from that of undoped SnSe, suggesting a higher probability of significant Fe concentration. The results are presented in Figure 6. The SEM image demonstrates that the surface of the disc-shaped flakes is smooth and homogeneous, indicative of uniform growth during the deposition process.

The EDX maps provide a detailed view of the elemental distributions within the flakes. Specifically, the top panel in Figure 6 shows the distributions of Sn and Se, respectively,

highlighting the primary composition of the flakes. The bottom panel presents the Fe distribution, in addition to the distributions of O and Si, corresponding to the substrate material. The Fe concentration was below the detection limit of EDX. This suggests that while Fe doping has a significant impact on the morphology of the SnSe structures, its actual concentration within the flakes is too low to be detected with EDX.

The ratio of Sn to Se was found to be $\text{SnSe}_{0.84}$ in the investigated sample. These results indicate slight deviations from the stoichiometric ratio of SnSe, which could be attributed to the influence of Fe doping and the specific conditions of the deposition process. The slight variations in the Sn ratio suggest that Fe doping might be causing some level of non-stoichiometry, potentially impacting the electronic and structural properties of the material.

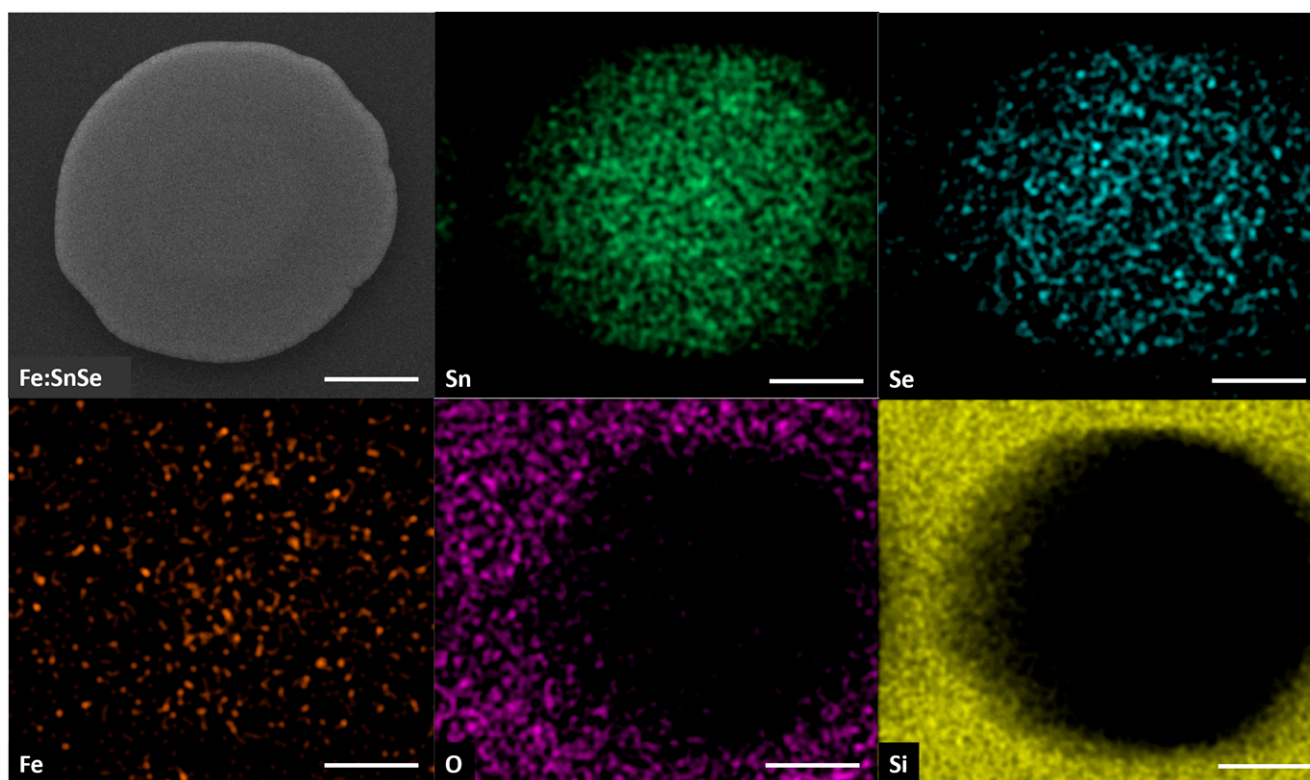


Figure 6. SEM image and elemental distribution maps obtained by EDX of a disc-shaped Fe-doped SnSe flakes. The scale bar is 8 μm .

3.3. Raman Measurements

Detailed investigation of SnSe flakes of various shapes, obtained from source material composition no. 3, was conducted using micro-Raman spectroscopy with a laser spot size of a few μm^2 and a monochromatic wavelength of 632.8 nm. Figure 7 presents the recorded micro-Raman spectra. The experimental Raman maxima for an undoped SnSe flake is shown in each panel, for comparison, and corresponds to the in-plane vibrational mode (B_{3g} at 109.9 cm^{-1}) and out-of-plane vibrational modes A_g^1 (71 cm^{-1}), A_g^2 (131.8 cm^{-1}), and A_g^3 (150.5 cm^{-1}). Another vibrational mode (B_{1g}) has two Raman-active components at 57 and 133 cm^{-1} , which were not experimentally detected in our undoped SnSe sample [24].

Upon careful analysis of the Raman spectra from different regions of the disc-shaped flakes (Figure 7a), it is generally observed that these spectra do not show significant changes compared to the Raman spectrum of undoped SnSe flakes. Variations are mostly related to the intensity of specific peaks and slight shifts in their positions. However, exceptions are noted in certain areas of some disc-shaped flakes. For instance, the Raman spectra in some regions display peaks shifted to 61.8 , 98.2 , 121.6 and 156.6 cm^{-1} , as observed in

spot 2 of Figure 7a(iii). In other areas, the shifted peaks coexist with those characteristic of the majority of Fe:SnSe flakes, as seen in spot 3 of Figure 7a(iii). These shifts are consistent across all cases and, interestingly, appear to be independent of the specific transition metal involved, as similar shifts are observed in disc-shaped Cr:SnSe. These observations lead us to propose the hypothesis that these could be resonant Raman spectra (RRS) [28]. For RRS to occur, the energy of the exciting radiation (1.96 eV) must be close to the allowed optical transitions (excitons) of SnSe. According to the data of Ref. [29], SnSe exhibits D excitonic series at ~ 1.83 eV. If, at high transition-metal doping levels, the transitions associated with D excitons shift to ~ 1.96 eV (the energy of the exciting radiation), resonant Raman-scattering processes could occur. This could render B_{1g} (~ 62 cm^{-1}) [24], B_{2u} (~ 98 eV, an infrared-active mode) [24], and B_{1u} (~ 122 eV, an infrared-active mode) [24] Raman active. It is important to note that the corresponding Raman peaks for FeSe occur at 179.8 cm^{-1} (A_g^1) and 193.9 cm^{-1} (B_{1g}) [30].

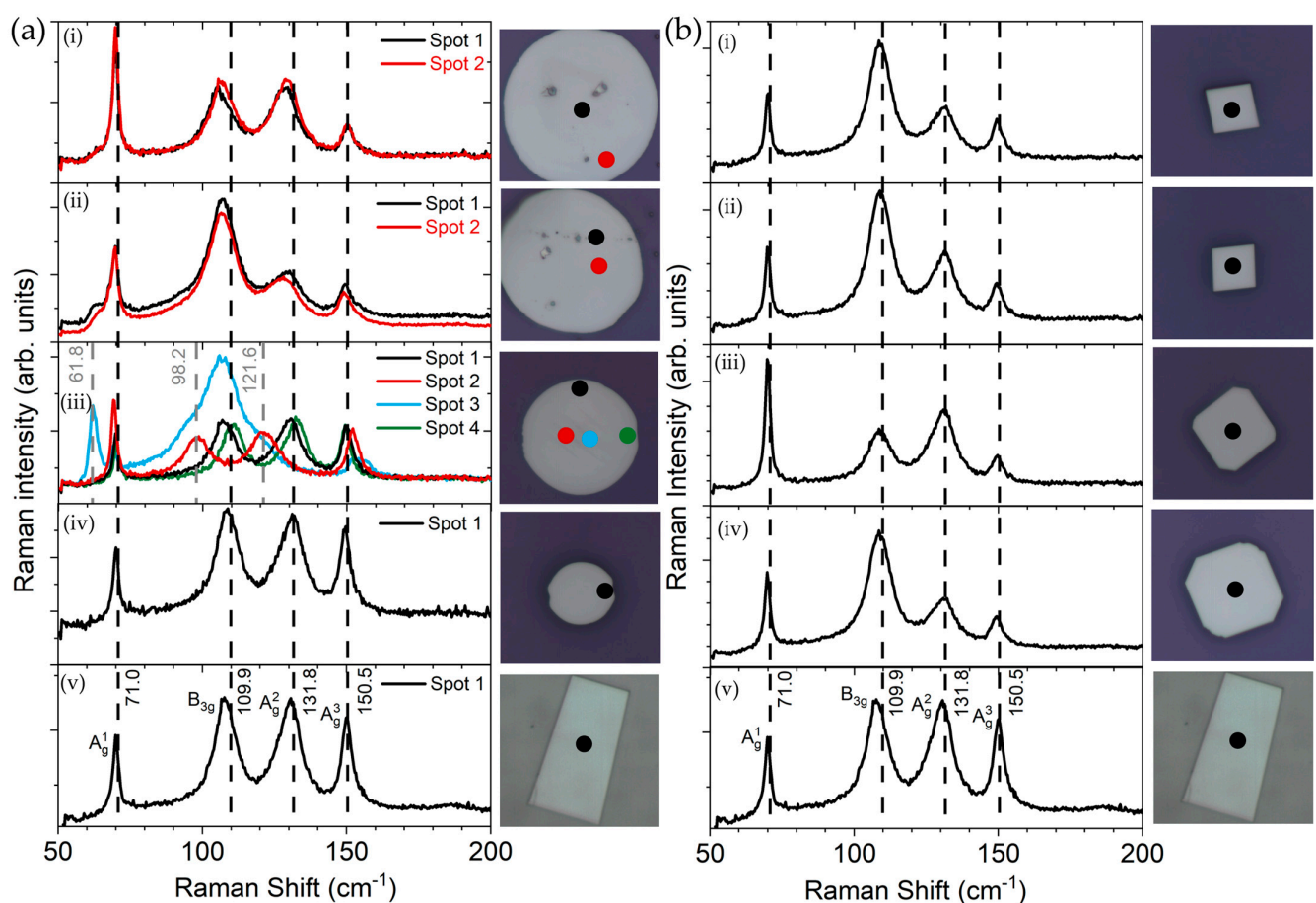


Figure 7. Micro-Raman spectra recorded on different areas of Fe-doped SnSe (a) disc-shaped (i–iv) and (b) rectangular shaped (i–iv) flakes obtained on the SiO_2/Si substrate using source material composition no. 3. Optical microscopy images of the investigated flakes and spots are shown next to each graph. Raman spectrum recorded on an undoped SnSe flake (v) is included in each panel, for comparison.

In Figure 7b, we observe that for square-shaped flakes, the positions of the Raman maxima remain unchanged, with variations observed only in their relative intensities. This trend is also present in disc-shaped flakes, suggesting that the effect is less related to local structural changes. This implies that the basic crystal structure of SnSe is largely preserved in these regions, despite the presence of Fe doping. The variation in the shape of the flakes suggests a gradual symmetry-breaking process during growth. It is likely that each flake comprises several crystallites, with varying horizontal and vertical extents,

creating boundaries that limit the occurrence of certain modes of vibration. Changes in the electronic environment induced by Fe doping could also be a contributing factor. Fe atoms substituting Sn in the SnSe lattice introduce localized distortions due to the difference in atomic radii and electronic configurations between Fe and Sn atoms. This substitution leads to the formation of localized magnetic moments and alters the vibrational properties of the lattice. The presence of Fe can also induce charge transfer between Fe and the surrounding SnSe matrix, further modifying the phonon modes [31]. Such variations in Raman intensities are common in two-dimensional materials, where changes in layer number, strain, and defects can significantly affect the scattering cross-section of different vibrational modes [32].

Moreover, the uniformity in the positions of the Raman peaks suggests that low Fe doping does not introduce new vibrational modes within the detection limits of the Raman setup, and the primary impact of Fe is on the existing modes. This observation is consistent with previous studies on transition-metal doping in 2D materials, where the introduction of dopants leads to intensity variations rather than shifts in peak positions. Such behavior can be linked to the localized nature of dopant interactions, which alter the electronic environment and scattering efficiency without significant changes in the overall lattice dynamics [33].

3.4. XPS

The chemical bonds between elements (Sn, Se and Fe) on the surface of the flakes obtained on the SiO₂/Si substrate using source composition no. 3 were investigated using XPS. Experimental XPS data (blue circles), with the fitted line (black) and individual components (colored lines) for each spectrum are shown in Figure 8. Voigt profiles were used for deconvolution, and all spectra had the inelastic background subtracted, using the Shirley profile.

The XPS results indicate the presence of Sn-Se and Fe-Se bonds on the surface of the flakes, as well as Sn-O, Fe-O bonds, and unreacted selenium. Given that different widths were used for the Sn 3d and Fe 2p components, relative concentrations were calculated for each element, after correcting the Voigt profile widths.

In the Sn 3d spectrum (Figure 8a), the SnSe component is at a binding energy of 485.3 eV, representing approximately 16% (Figure 8c) of the Sn on the sample surface. The main photoemission line of Fe overlaps with Sn 3p^{3/2}. To identify the oxidation state of iron, we also presented the spectrum after excluding this contribution (purple line). Thus, the only Fe oxide obtained on the surface is FeO, recognizable by its satellite shape and the large distance from the first component characteristic of this oxidation state [34]. Besides FeO, there is also a 7% contribution of an Fe-Se compound at a binding energy of 707.3 eV. This compound is also found in the Se 3d spectrum at 52.2 eV (Figure 8b). The Se 3d spectrum comprises six components, among which Fe-Se represents ~8%, SnSe approximately 25%, and Se²⁻ surrounded by defects ~27%. Secondary compounds, Se⁰ and adsorbed/Se⁰, account for the remaining ~40%.

The O 1s spectrum (Figure 8d) is dominated by O-Si, and, due to similar binding energies (approximately 530 eV), distinguishing between O-Fe and O-Sn was not possible. The sum of these components is approximately 2%.

The confirmation of the presence of Fe-Se bonds on the surface of the flakes was confirmed, providing direct evidence of successful Fe incorporation into the SnSe lattice, contributing to the observed variations in morphology. Despite the relatively low overall Fe concentration detected, the presence of these bonds highlights the effectiveness of our doping process and its impact on the material's characteristics.

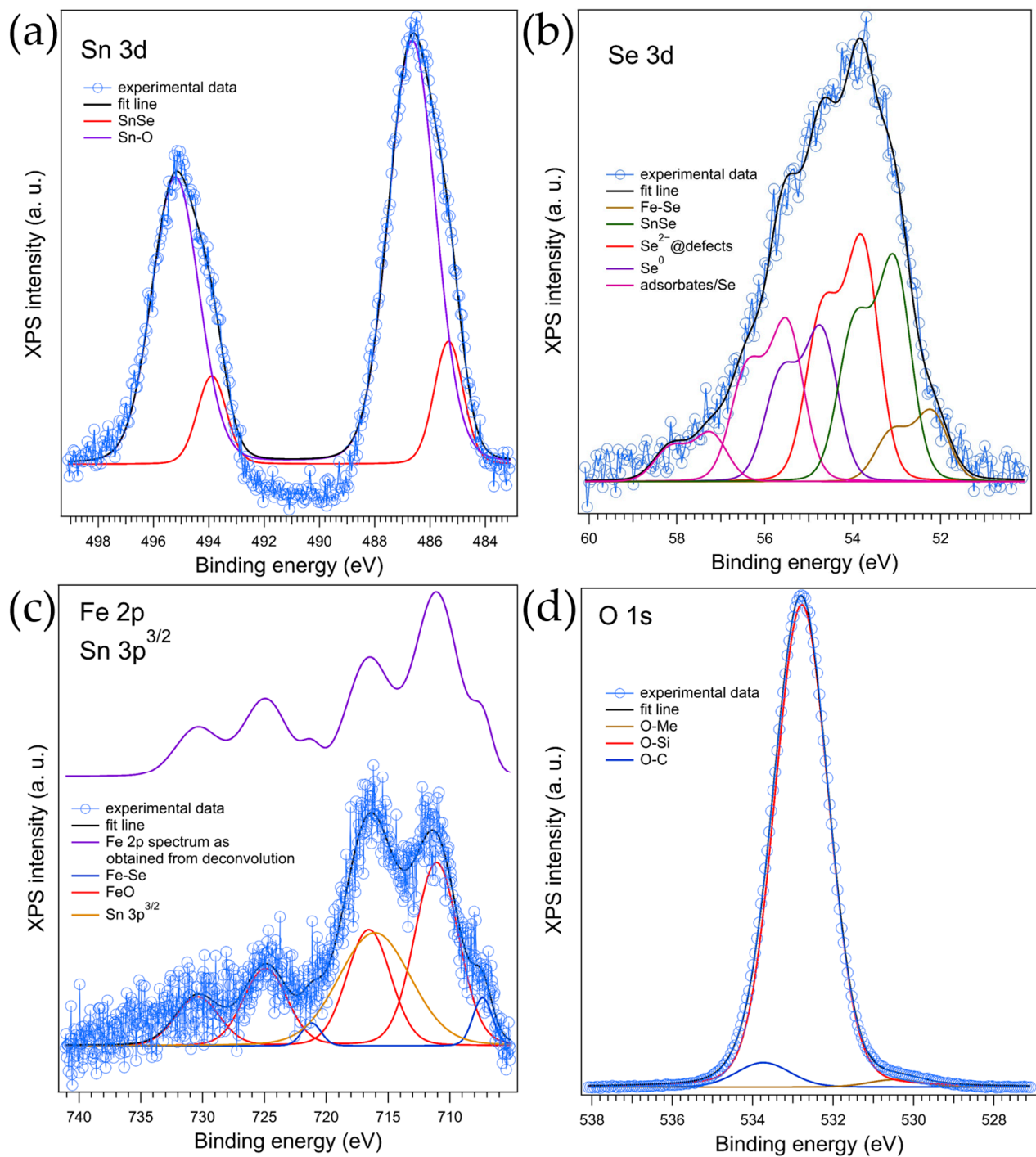


Figure 8. XPS analysis results for the lines of interest: (a) Sn 3d, (b) Se 3d, (c) Fe 2p (overlapping with Sn 3p^{3/2}). The Fe2p spectrum is also represented on top, in purple, for a better visualization of the difference between the fit line and the Sn 3p^{3/2} component. (d) O 1s.

3.5. Electrical Characterization

Memristive devices were built with the flakes obtained using source composition no. 3 following the same steps described previously [35]. The electrical characteristics of a device are shown in Figure 9. Initially, the memristor behaves as a semiconductor in a low-resistance state (i). Therefore, the SnSe flakes behave as diluted magnetic semiconductors, as the Fe concentration (evidenced by XPS measurements) is sufficient to maintain the semiconductor character of SnSe. At a reset voltage of 1.6 V, the device switches (the current

drops abruptly) to a high-resistance state (ii), which is maintained (iii) until applying a reverse bias voltage of -1.6 V, when the memristor reverts to the low-resistance state (iv). This symmetric memristive behavior is stable, maintaining over 20 set/reset cycles. Several of them are shown in Figure 9, with the median cycle being bolded.

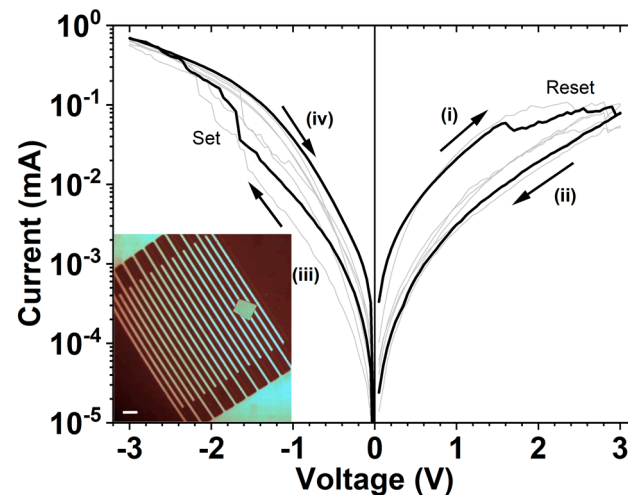


Figure 9. Current–voltage (I–V) characteristics of one of the Fe-doped SnSe memristive devices. The current is represented in absolute value. Initial low-resistance state (i), followed by high-resistance state after reset at 1.6 V (ii) and (iii), and set to low-resistance state at -1.6 V (iv). The median cycle is evidenced in bold. Inset shows the optical image of the memristive device, with a scale bar of $20\ \mu\text{m}$.

The switching mechanism in these Fe-doped SnSe memristive devices is due to defect-mediated processes. In this scenario, defects migrate toward grain boundaries under the influence of an external electric field, forming low-resistance channels. This migration dynamically adjusts the Schottky barriers between the SnSe flakes and metal electrodes, leading to changes in resistance. Specifically, the accumulation of chalcogen vacancies near the grain boundaries during the set and reset processes induces conductance changes, facilitating the memristive switching behavior [36,37].

In the case of SnSe, Fe doping introduces localized distortions and atomic vacancies that act as dopants. These vacancies migrate through the grain boundaries under the influence of an electric field, modifying the electronic properties of the material. The dynamic tuning of Schottky barriers by migrating defects results in reversible switching between high- and low-resistance states. This behavior allows for stable and repeatable switching cycles.

Furthermore, SnSe flakes exhibit anisotropic electrical conductivity, with the highest conductivity along the zigzag direction and a secondary peak along the armchair direction [38]. This anisotropy means that electrical conductivity is significantly lower along the a -axis, being approximately ten times smaller. Consequently, lateral memristors are preferable to vertical devices, due to their enhanced performance in terms of electrical conductivity and overall efficiency [39].

In our previous study on undoped SnSe nanoflakes [9], the memristive devices demonstrated a threshold voltage of 3 V with an operating current of 0.1 mA, primarily driven by a defect-migration mechanism. These devices were characterized by relatively low power consumption, making them competitive with other transition-metal dichalcogenide memristors. In contrast, the current study on Fe-doped SnSe memristive devices, which are also built from rectangular flakes similar to the undoped SnSe devices, reveals several significant differences. The Fe-doped devices exhibit a lower threshold voltage of 1.6 V, but a significantly higher operating current of 0.7 mA. The incorporation of Fe into the SnSe matrix introduces chalcogen vacancies and localized distortions that enhance the memristive switching behavior. These defects and distortions facilitate dynamic tuning

of Schottky barriers, which is important for the observed stable and repeatable switching between high- and low-resistance states.

In addition, Bi-doped SnSe memristors, as reported recently [22], exhibit ferroelectric memristive behavior driven by ferroelectric polarization and conductive filament formation. In contrast, our study on Fe-doped SnSe memristors did not measure ferroelectric properties directly, but focused on defect-mediated switching mechanisms. The Fe doping leads to a different type of memristive behavior, primarily influenced by chalcogen vacancies and defect migration. This mechanism is distinct from the ferroelectric switching observed in Bi-doped SnSe.

While we have not yet explored the potential magnetic properties of Fe-doped SnSe, the introduction of Fe atoms into the SnSe matrix could lead to further studies on multifunctional devices combining memristive behavior with possible magnetic functionalities. Future work could explore these aspects, providing a broader understanding of the material's capabilities.

4. Conclusions

In this study, we successfully obtained and characterized Fe-doped SnSe semiconductors, using an optimized CVD method, and integrated them into memristive devices. The incorporation of Fe into SnSe resulted in diverse-shaped flakes, including rectangles, discs, stripes, and wires. Micro-Raman spectroscopy revealed significant shifts in vibrational modes, indicating structural changes due to Fe doping, while XPS further confirmed the presence of Sn-Se and Fe-Se bonds. The memristive devices exhibit stable and repeatable switching behavior between high- and low-resistance states, driven by a defect-mediated mechanism. The introduction of Fe induces chalcogen vacancies and localized distortions that facilitate resistance changes through dynamic tuning of Schottky barriers. The anisotropic electrical conductivity of SnSe further enhances the device performance, making it a promising candidate for advanced memory and computing applications. The observed electrical characteristics confirm the influence of Fe doping in achieving the desired memristive properties while maintaining the semiconductor nature of SnSe. Further research is needed to fully characterize the Fe-doped SnSe flakes including the band gap, carrier concentration, and intrinsic electrical properties of these materials and the endurance and retention properties of the memristive devices, as well as to explore potential optimizations in doping and device architecture.

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