

Research Progress and Applications of 2D Antimonene

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Abstract: Antimonene has attracted much attention due to its excellent properties such as high carrier mobility, excellent thermoelectric performance and high stability. In order to verify its theoretical advantages, a large number of experimental studies have been carried out and its applications explored. This paper mainly introduces the experimental preparation of antimonene by mechanical exfoliation, liquid phase exfoliation and epitaxial growth, summarizes the advantages and disadvantages of each method, and describes the applications of antimonene in sensor, battery, medicine and laser. Finally, prospects have been made to the future applications of antimonene in photoelectric field.

Keywords: antimonene; mechanical exfoliation; liquid phase exfoliation; molecular beam epitaxy

1. Introduction

As silicon transistor size decreases continuously according to Moore's law and gradually approaching its physical limit, new devices are proposed to suppress the short-channel effect, such as Fin Field Effect Transistor (FinFET) and Gate All Around (GAA) transistor. In addition, the two-dimensional material, an all-new material, is a promising channel material due to its excellent gate control capability [1]. Two-dimensional materials (2D) are typically thinner than the mean free path of most particle transport, including phonon, electron and exciton, which forces them to follow ballistic transport. This quantum confinement effect fundamentally alters the electronic properties of two-dimensional thin film materials, which are ideal for basic research and new electronic applications. Since graphene was successfully isolated in 2004 [2], two-dimensional materials have attracted wide attention. However, graphene's zero-band gap disadvantage makes it challenging in switching devices of transistors. Subsequently, graphene-like layered structures, such as molybdenum disulfide [3], boron nitride [4], and silicene [5], attracted researchers' attention. For the transition metal-sulfur compound with band gap, the theoretical carrier value is low and the carrier transport is badly scattered, resulting in the poor performance of the transition metal-sulfur compound transistor [6], so scientists turn their attention to main group V elements. In 2015, Li et al. [7] successfully prepared black phosphorus and proved that it has high carrier mobility, but its poor stability makes it difficult to be applied in devices.

Zhang et al. [8] first reported the theoretical research results of the layered materials: antimonene, whose band gap changes from metal to semi-metal, and the single-layer antimonene, that has a large band gap of 2.28 eV. Subsequently, the study of antimonene attracted people's attention. Antimonene, which has high carrier mobility [9–11], stability [12], excellent thermoelectric performance, large band gap and spin orbit coupling, has great potential for electron, photoelectron and spintronic development [13,14]. The mechanical and electronic properties of monomolecular membrane of antimonene can also be regulated by uniaxial and biaxial tensile strain [15–17]. Under tensile strain, antimonene can be transformed from an indirect band gap semiconductor to a direct one, or



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even semi-metal [18,19]. Especially under strong electric field, their band gap gradually closes due to the field-induced motion of near free electron states [20]. It is found that antimonene can be tuned to a two-dimensional topological insulator (TI) under anisotropic in-plane strain by first-principle calculation [21]. The tunable bulk gap makes antimonene a material of choice for achieving the quantum spin Hall effect (QSH) at high temperatures, meeting the requirements of future low-power electronic devices [22] and converting β -Sb bilayer from semi-metal to superconductor through electron doping [23]. It has nonlinear characteristic behavior in optical properties [24,25], and has applications in laser [26,27] and laser protection [28]. The theoretical research of antimonene has been very mature, but its experimental preparation is still worthy of further exploration. At present, the real single-layer preparation of antimonene thin films prepared in the laboratory has low yield and small size, which limits the experimental verification and practical application of antimonene.

In this paper, we will analyze the mechanical exfoliation and liquid phase exfoliation methods and molecular beam epitaxy for the preparation of antimonene and study the factors affecting the preparation of antimonene and explore the rules for the preparation of antimonene to provide a reference for the next-stage experimental preparation of antimonene and summarize the applications of antimonene in sensing and medicine, especially the huge potential application in the photoelectric field.

2. Theoretical Research and Experimental Methods

2.1. Theoretical Research

Antimonene with different thickness has different electronic structure and optical properties, depending on its thickness. CHEN Wen et al. [18] studied the properties of 1–4 layers of antimonene through first principle, and the results showed that 1 L and 2 L have indirect band gaps by using PBE, HSE, and modified Van der Waals (FDT-2), and 3L and 4L exhibit metal properties. At the same time, its reflection and absorption capacity were analyzed. The reflection spectrum is shown in Figure 1a. The emission coefficient increases with the increase in layers, but the focusing appears between 4–6 eV. The absorption coefficient is shown in Figure 1b. With the increase in layers, the peak value of the absorption curve redshifts, indicating that the larger the layer, the smaller the band gap. When the antimonene is transformed from antimonite to single-layer antimonene, its absorption peak moves from the visible region to the ultraviolet region, and the absorption of the ultraviolet region is greater than that of the longer wavelengths. According to the reflectance δR [29] and the absorbance (A) of the substrate and material with the refractive index of n_{subs} , the following relationship holds:

$$\delta R(\lambda) = \frac{4}{n_{subs}^2 - 1} A(\lambda) \quad (1)$$

When the substrate is in the same medium, n_{subs} can be regarded as constant, that is, the reflection coefficient is related to the absorbance of the material. For two-dimensional materials, the absorbance of the material generally increases with the increase in the layer, that is, the reflection coefficient also increases.

In 2015, Wang et al. [30] theoretically calculated the stability of antimonene. The α -phase Sb has two sublayers, and the atoms of the same layer are in different planes. The β -phase antimony structure is hexagonal lattice with curved surface. The stability of antimonene is studied by calculating phonon dispersion curve. The antimony phonon dispersion curves of α and β phases have no hypothetical vibrating mode, which indicates their good stability, while the antimony of γ and δ phases have virtual mode, indicating that their structures are not stable.

S Wang et al. [31] calculated the thermal conductivity of antimonene from ab initio by combining the Boltzmann transport equation of phonons. The results showed that the lattice thermal conductivity of antimonene was 15.1 W/mK at 300 K, indicating that the low thermal conductivity of antimonene was caused by its small group velocity, low Debye

temperature and high flexion. Gupta et al. [32] also calculated the thermal conductivity of α and β phase antimonenes theoretically, and at the same temperature and rough edges, α has better thermally conductivity than β -phase antimonene, which is attributed to the difference in phonon energy spectrum and group velocity. The thermoelectric materials can use the thermoelectric effect to convert the waste electricity into electric energy, so antimonene has the application potential of the thermoelectric materials.

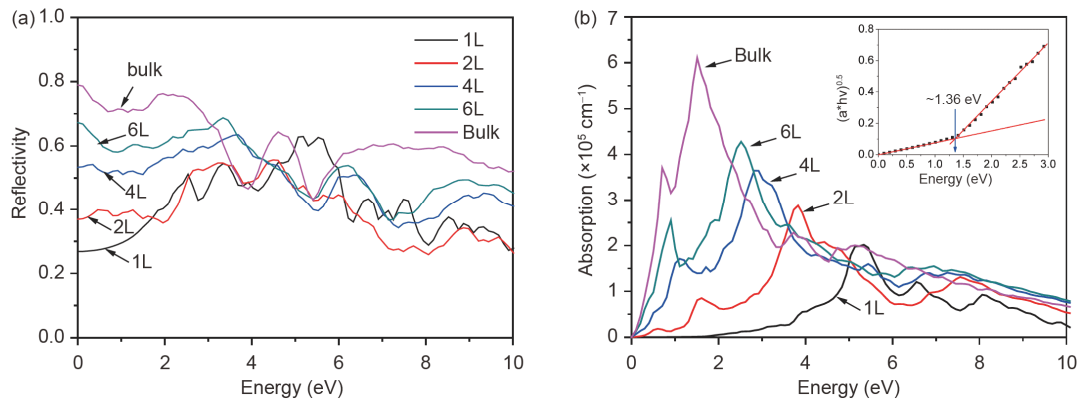


Figure 1. Reflectance of a layer of antimonene and antimonite material: (a) reflectance spectra; (b) absorption spectra (upper right illustration is the energy band value of single-layer antimonene estimated by the “Tauc” method). Reprinted with permission from Ref. [18]. Copyright 2021, Science China Press.

In 2018, Shi et al. [33] calculated the electron transport characteristics of β -phase antimonene nanoribbons (Z-SbNRs) based on the density function theory and non-equilibrium Green’s function, and found that the length and width of the central scattering region have a great influence on the electron transport of antimonene. Under the same voltage, the current increases with the increase in the width of the band and decreases with the increase in the length. In 2020, Xie et al. [34] also studied the electron transport characteristics of antimonene nanoribbons through first principles. The bent and folded antimonene nanoribbons treated with edge hydrogenation have a large semiconductor band gap, and the current is almost zero at the low bias pressure of 0–0.8 V. The conductance of antimonene nanoribbons treated with edge oxidation was significantly increased, and the adjustable negative differential resistance behavior was detected.

As early as the 1980s, antimony has been experimentally studied on conductor substrates [35–37] through the evaporation of antimony by filament or liquid pool, and the growth of antimony films were mainly on GaAs (110), and the study of its electronic properties (band gap) was carried out using STM and Raman spectroscopy. Due to the influence of surface layer coupling, the research has been hindered. From 2016, the experimental preparation of antimonene has been using mechanical exfoliation, liquid phase exfoliation and molecular beam epitaxy.

2.2. Mechanical Exfoliation

In order to obtain high quality single or multilayer nanocrystals from natural multilayer structures or substrates, mechanical exfoliation and transfer techniques have been developed, which involve interfacial exfoliation and intraformational tearing processes [38]. In two-dimensional material exfoliation, this method has also received much attention.

Ares et al. [39] prepared single-layer and few-layer antimonene sheets by an improved mechanical exfoliation method in 2016. The antimonene was first transferred by tape to a thin layer of an elastic polymer. The softness of the viscoelastic polymer resulted in a higher yield of thin sheets on the polymer surface. The process and appearance of the stripped antimonene by pushing the polymer onto the silicon oxide substrate are shown in Figure 2. The average thickness of the antimonene is in nanoscale and the antimonene has

stepped properties. It is also proved that the antimonene is of the β -phase structure with good stability.

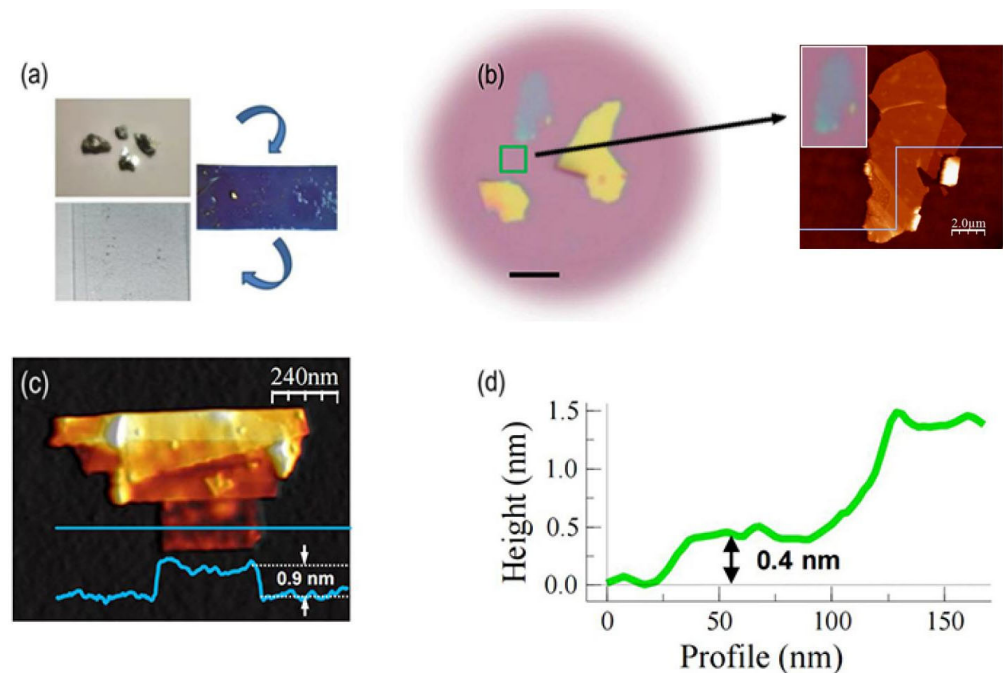


Figure 2. (a) Exfoliation process of antimonene; (b) optical microscope images. The illustration is a larger view of the green box; (c) AFM appearance map; (d) the minimum thickness of the peel is 0.4 nm. Reprinted with permission from Ref. [39]. Copyright 2016, John Wiley and Sons.

Since few-layer antimonene cannot be measured by Raman spectroscopy, Ares et al. [40] proposed to measure few-layer antimonene using optical microscopy and atomic force microscopy, to measure the thin slices using wavelengths in the visible spectrum, and then quantitatively interpret the optical contrast using a model based on Fresnel's law to obtain the refractive index and absorption coefficient of these thin crystals in the visible spectrum. Thus, the optical microscope data can be quantitatively analyzed to determine the thickness of the sheet in a rapid and nondestructive manner.

Fickert et al. [41] prepared antimonene nanosheets with a thickness of 14 nm by mechanical exfoliation method in 2020. First, the high-viscosity film is used to gently press the new cutting surface of antimony crystal, then the mucous membrane is pressed on the same mucous membrane, the process is repeated, and then the adhesive film containing thin antimony microcrystals is pressed on the SiO_2/Si substrate.

2.3. Liquid Phase Exfoliation

In 2008, graphene was successfully prepared for the first time by liquid phase exfoliation, in which a suitable solution was selected to remove the two-dimensional material [42]. This method has been used to study the preparation of antimonene since it was successfully stripped.

In 2016, Gibaja et al. [43] prepared antimonene with thickness multiple of 4 nm in isopropyl alcohol:water (4:1) mixture. The grinding antimony crystals were ultrasonically cleaned at 400 K for 40 min, and then centrifuged at 3000 rpm for 3 min. AFM (Atomic Force Microscope) measurement showed that the thickness was a multiple of 4 nm and the area was 1–3 μm^2 , as shown in Figure 3. However, the end of the sheet appears to be somewhat damaged, possibly due to solvent contamination, and it is noted that Raman spectrometric measurements depend on the thickness of antimonene. In 2019, they [44] studied the effects of grinding, solvent and ultrasound on the preparation of antimonene. Antimonene nanosheet samples were prepared, approximately 50% of which had a height

of 2–10 nm and a transverse size of 40–300 nm. The antimony was ground by wet ball method and treated with 400 W tip ultrasound for 40 min in 2-butanol (NPM:H₂O = 4:1) and centrifugated at 3000 rpm for 3 min, as shown in Figure 4. Three methods of grinding antimony crystal, dry ball grinding antimony crystal and wet ball grinding antimony crystal were compared. Through SEM (scanning electron microscope) analysis, the crystal obtained by wet ball grinding in butanol has larger transverse size and smaller thickness and the highest suspension concentration. Wet ball grinding method and the same ultrasonic and centrifugal methods were used to compare the influence of solvents, and Figure 5 shows the peel values of different solvents. In NPM:H₂O = 4:1, the concentration of the peel is approximately 0.368 g·L⁻¹, which is 30 times higher than the previous suspension concentration [45]. In butanol, however, there will be a higher DA value (DA: ratio between size and height value). At the same time, the effect of ultrasonic tip and ultrasonic bath on concentration and DA were compared, and the results showed that the tip ultrasound was better. The influence of different conditions on the preparation of antimonene in liquid phase separation and its better conditions were explored.

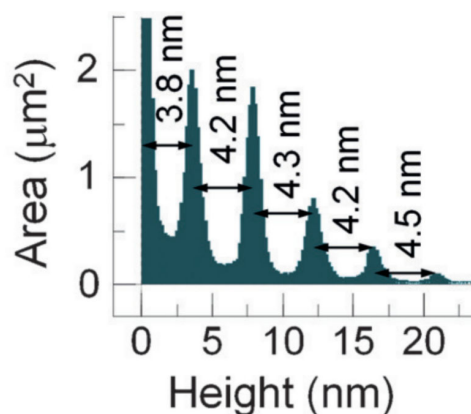


Figure 3. Height and size of antimonene prepared. Reprinted with permission from Ref. [43]. Copyright 2016, John Wiley and Sons.

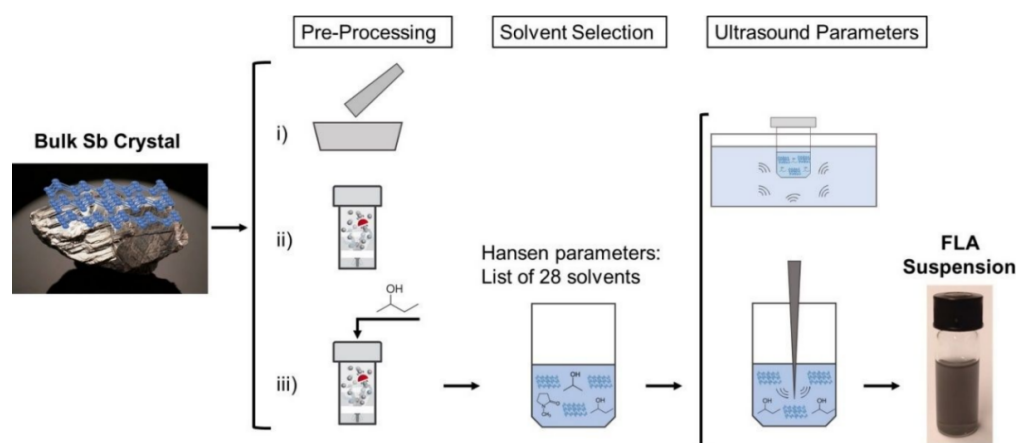


Figure 4. The liquid phase exfoliation process of antimony is summarized, including the different steps. Firstly, different methods are used for pretreatment: (i) grinding bulk antimony crystals; (ii) dry ball milling bulk antimony crystals; (iii) wet ball milled bulk antimony crystals. Secondly, the solvent was selected based on the parameters using 28 different solvents, and thirdly, the ultrasound parameters were compared, including bath ultrasound and tip ultrasound. Arrows highlight the best route to obtain layers of antimonene with the highest concentration. Reprinted with permission from Ref. [44]. Copyright 2019, Royal Society of Chemistry.

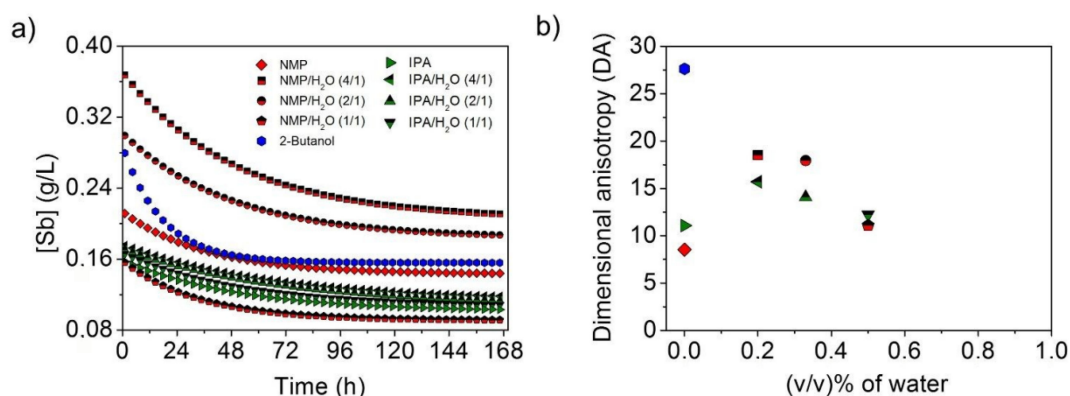


Figure 5. (a) The concentration of antimonene in the suspension after centrifugation $[Sb]$ ($\text{g}\cdot\text{L}^{-1}$), plotted with the precipitation time of the sample prepared with the solvent described in the legend; (b) the relationship between the DA ratio of antimonene nanolayer and the volume fraction (%) of water in the solvent mixture. Reprinted with permission from Ref. [44]. Copyright 2019, Royal Society of Chemistry.

In order to reduce the thickness of antimonene thin films, Gao et al. [46] prepared antimonene with a thickness of less than 2 nm and a transverse size of approximately 3 μm by liquid-phase exfoliation method through pressure alloying. Through hydrothermal reaction using chemically active n-butyllithium, stable Li_3Sb phase was formed at the edge of β -phase Sb, and then reacted with water to form gaseous SbH_3 , thus promoting the subsequent separation. When the hydrothermal reaction is carried out at atmospheric pressure, antimonene cannot be spalled off. However, when the pressure is too high, only antimonene fragments can be obtained. Large-sized antimonene can be obtained only when 14 mL n-butyllithium is placed in a 50 mL of autoclave at 80 $^\circ\text{C}$, as shown in Figure 6.

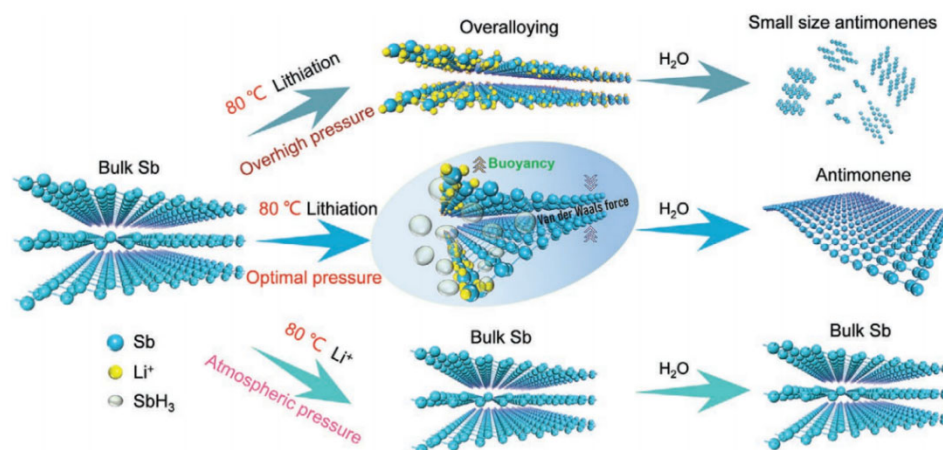


Figure 6. Schematic diagram of liquid phase separation for pressure alloying. Reprinted with permission from Ref. [46]. Copyright 2021, John Wiley and Sons.

In order to study the experimental conditions of antimonene film thickness, antimonene films with adjustable thickness were prepared. By changing the centrifugal speed from 1000 rpm to 9000 rpm, Wang et al. [47] prepared antimonene with a thickness of 0.5–7 nm. The antimonene crystals were ground in 2-butanol and ultrasonic cleaning was carried out in 2-butanol solvent with tip ultrasonic device. The thickness of antimonene was approximately 5–7 nm at the low centrifugal speed range of 1000–2000 rpm. When the centrifugal speed is 2000–5000 rpm, the thickness of antimonene is approximately 2–3 nm. When the centrifugal speed is increased to 5000–9000 rpm, the thickness of antimonene is reduced to approximately 0.5–1.5 nm. When the centrifugal speed is increased to

9000 rpm, homogeneous antimonene quantum dots with a size of 20–30 nm and a thickness of 0.3–1 nm are formed.

Besides the influence of centrifugation, grinding and solvent, the ultrasonic power and ultrasonic cleaning time also affect the preparation of antimonene. For example, Zhang et al. [48] prepared antimonene nanosheets with a thickness of 0.6 nm and transverse size of $0.55 \pm 0.36 \mu\text{m}$ by extending ultrasonic cleaning time. Lin et al. [49] prepared antimonene with a thickness of approximately 0.5 nm and a transverse size of approximately 700 nm through high Hypersonic waves and high power.

Grinding antimonene, centrifugal speed, ultrasonic and solvent all have influences on the preparation of antimonene. Wet ball grinding, high centrifugal speed, high power ultrasonic for a long time and surface energy matching solvent are more conducive to the preparation of antimonene with lower thickness. Grinding the antimony powder first is beneficial to the exfoliation of antimony. The grinding of antimony powder provides shear force on the surface of Sb layer. Compared with mechanical exfoliation method, the grinding of antimony powder provides shear force on the surface of Sb layer in a more controllable way, promotes the transverse spalling, thus producing a larger and thinner antimony film, and avoids the longitudinal destruction of antimony film atoms. Ultrasound and centrifugation also have great influence on the preparation of antimonene. Since ultrasound can provide energy to break the van der Waals interaction between the antimony atomic layers, together with grinding, they are beneficial to produce thin antimony film. Grinding with high power ultrasonic wave or prolonged ultrasonic time are aimed at exfoliation with higher concentration and thinner antimonene. However, different centrifugal speeds can produce antimonene with different thicknesses. For example, Wang et al. [47] prepared antimonene thin films with thickness of 0.5–7 nm at different centrifugal speeds. Antimonene can be exfoliated in a variety of solvents. When the surface energy of the solvent matches the surface energy of the stripped layered crystal, the energy cost is lowest and the concentration of the suspension is maximized. When the surface tension of the solvent is in the range of $23\text{--}42 \text{ mJ}\cdot\text{m}^{-2}$, the concentration of the suspension increases. Gibaja et al. [44] proposed that suspension of antimonene has the highest concentration in NPM:H₂O = 4:1, but its DA value is lower than that of 2-butanol. In addition, antimonene can be stripped in ethanol, ethylenediamine and other solvents. The size of antimonene prepared by liquid phase exfoliation method is larger than that by mechanical exfoliation method, and the operation is simple and convenient, but its detection and contamination are easily affected by the solution.

2.4. Epitaxial Growth

In addition to mechanical exfoliation and liquid phase exfoliation, epitaxial growth is often used for multilayer and single-layer growth of two-dimensional materials. Epitaxial growth includes the bottom-up growth pattern, which is also useful for the experimental preparation of antimonene.

2.4.1. Preparation of Multilayer Antimonene

In 2016, Ji et al. [9] grew antimonene with thickness of 1–50 nm and transverse size of 5–10 μm on fluorophlogopite substrate by van der Waals epitaxy. It is also pointed out that the antimonene polygon has a conductivity of up to $10^4 \text{ S}\cdot\text{m}^{-1}$ and good optical transparency. The sample synthesis process is shown in Figure 7a, using a two-zone tubular furnace with separate temperature control. The antimony powder placed in the source area was heated to 660 °C to vaporize the antimony vapor. The fluorophlogopite substrate was placed in the downstream area at 380 °C. The synthesis process was kept for 60 min, then the furnace was cooled to room temperature. Figure 7b shows the growth pattern of antimonene on mica sheet. Figure 7c–f shows typical optical microscope image of several layers of antimonene sheets synthesized on a substrate with a scale of 5 μm . These antimonenes exhibit several polygonal shapes, including triangles, hexagons, diamonds, and trapezoids. As shown in Figure 7g, the thickness of antimonene polygons as low as 4 nm

(approximately 10 atomic layers) was observed with an atomic force microscope, and in fact, very small sheets of antimonene with transverse dimensions of approximately 100 nm and thickness as low as 1 nm (Figure 7h) were obtained. Microscopic study on HRTEM (High Resolution Transmission Electron Microscopy) and Raman spectroscopy showed that the obtained antimonene was a curved hexagonal structure β phase. Based on first principles and molecular dynamics calculations, the thermodynamic and kinetic stability of antimonene was illustrated. The air stability of antimonene and the thermodynamic stability of antimonene were demonstrated by the non-easy reaction between antimonene and oxygen. At the same time, the semiconductor parameter analyzer was used to characterize the electrical characteristics of antimony transistor. The surface antimony has good conductivity and current–voltage (I_{ds} – V_{ds}) characteristics at zero gate bias, and the I – V curve shows good ohmic performance. The resistance of 30 nm thick antimony device is 600 Ω , and the conductivity is $1.6 \times 10^4 \text{ Sm}^{-1}$. The conductivity change in antimonene device after 100 consecutive bendings was measured, and the conductivity decreased by only 4%, which proves its application potential as flexible transparent conductive electrode.

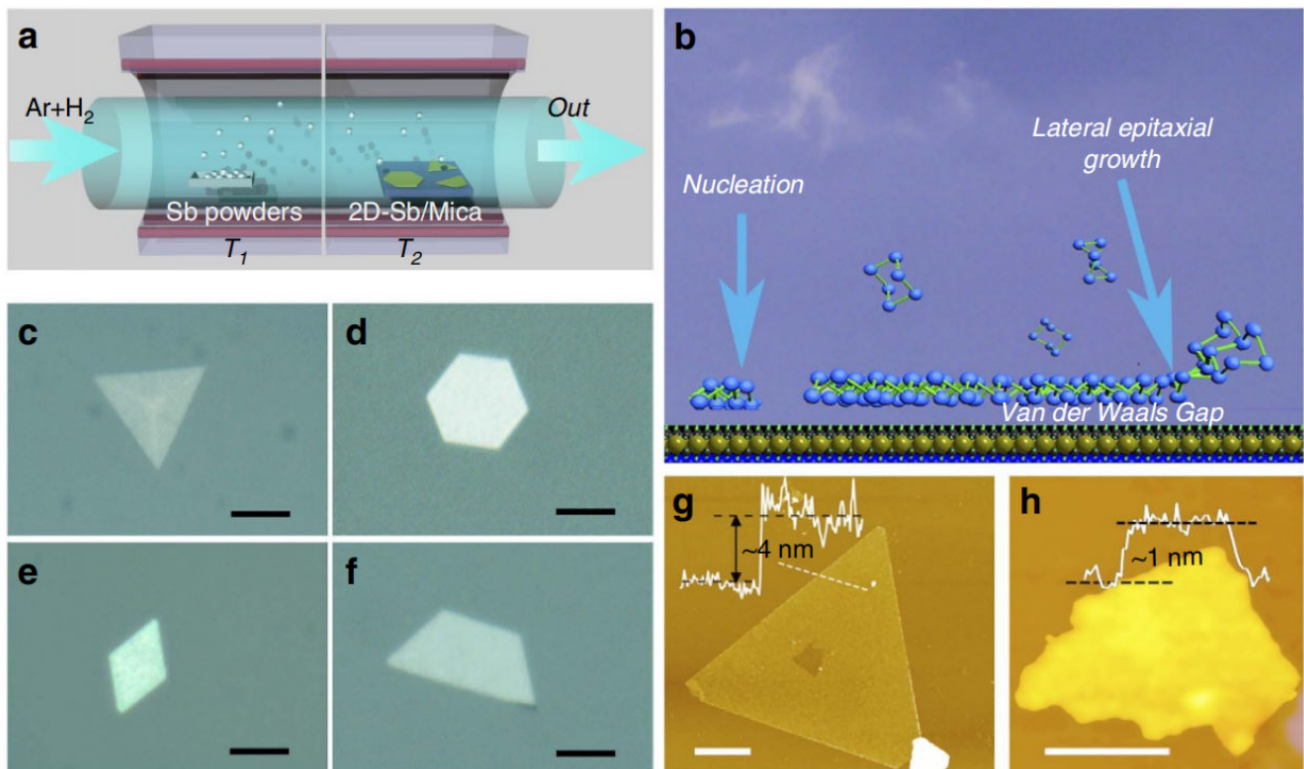


Figure 7. Synthesis of antimonene polygons on mica substrate by van der Waals epitaxy: (a) Schematic diagram of synthesis in tubular furnace; (b) schematic diagram of van der Waals epitaxial; (c–f) optical images of typical anti-monad polygons with triangular, hexagonal, rhombus and trapezoidal shapes, respectively. The scale is 5 μm ; (g) AFM images of typical triangular anti-monoene slices. The thickness is 4 nm. The scale is 1 μm ; (h) atomic force microscope image of microantimonene sheet. The thickness is approximately 1 nm. The scale is 50 nm. Reprinted with permission from Ref. [9]. Copyright 2016, Springer Nature.

In addition to van der Waals epitaxy, there is also molecular beam epitaxy. SH et al. [50] grew antimonene of 1–5 BL (BL is double layer) on $\text{Bi}_2\text{Te}_2\text{Se}$ substrate, while antimonene of 1 BL is rare; most of them are 2–5 BL antimonene, and the area of antimonene is tens of nanometers. STM (Scanning Tunneling Microscope) was used to observe the formation of 2, 3, 4, 5 BL layers of antimonene on $\text{Bi}_2\text{Te}_2\text{Se}$ substrate, with the area proportion of approximately 18%, 18%, 8%, 2%. To investigate the electronic structure of antimonene thin films, STS measurements were conducted. dI/dV curves were plotted along the lines

crossing the two adjacent edges. The results show that the charge transfer between the film and the substrate depends on the thickness of the film.

For two-dimensional materials with layered structure, it can also be used as a substrate for the growth of antimonene. In 2018, Chen et al. [10] grew a layered monocrystal antimonene film with a thickness of 17 nm and a size of 16.2 nm on the surface of MoS₂/sapphire. Two layers of MoS₂ were generated on the sapphire surface, and then the substrate was moved to the growth chamber, where the growth temperature was 200 °C for 60 s, and continuous antimonene films were synthesized, as shown in Figure 8. AFM and HRTEM were used to observe the appearance of antimony films. The adhesion of antimony at 200 °C is higher than that at room temperature. The monocrystal-oriented (012) antimony films were detected by XRD (X-ray diffraction). At the same time, multilayer antimony as contact metal for other 2D materials was studied. By using standard lithography, metal deposition and chemical etching, gold–antimony electrodes with different degrees of separation were prepared from antimony on MoS₂/Sapphire samples. TLM (transmission line) method was used to determine that the specific contact resistance of Au/antimony electrode was significantly reduced. Better performance can be obtained by using antimony as a contact metal for 2D devices. In 2019, Matthieu et al. [51] prepared antimonene with a thickness of 4–9 nm and a size of 1–3 µm on graphene/gel substrate. The antimony molecule used was Sb₄, and the weak interaction between antimonene and graphene was proved. LEED (low-energy electron diffraction) pattern was used to show that the growing layer had the crystal structure of β-antimonene, and the lattice constant was 4.28 ± 0.02 Å. AFM observed 2D islands and their appearance on the surface and analyzed the effect of deposition rate. LEEM studied the growth dynamics of antimonene, and the image showed that as the islands approached each other, the island binding decreased and the lateral growth rate decreased. It is shown that there is a large Sb₄ diffusion length (LD) on graphene, which promotes competition between growing islands.

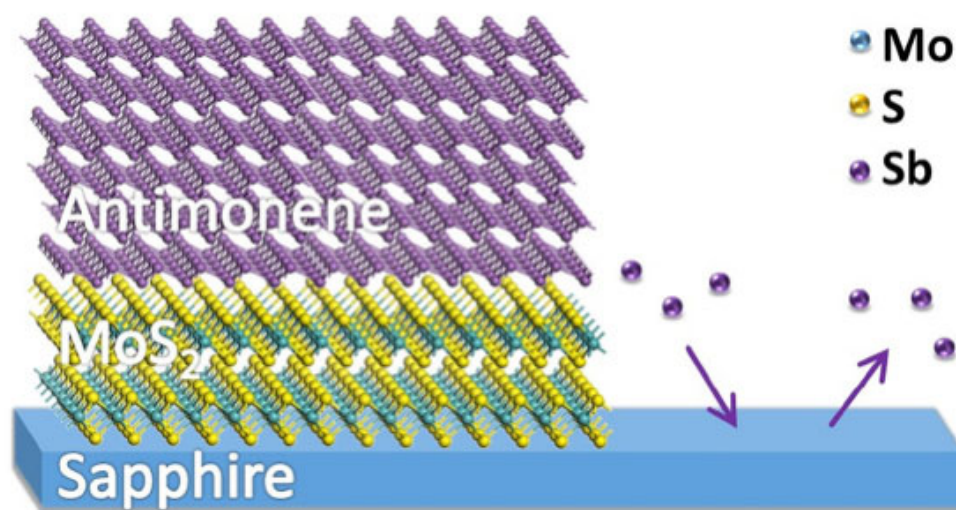


Figure 8. Growth of antimonene on MoS₂/sapphire. Reprinted with permission from Ref. [10]. Copyright 2018, American Chemical Society.

In addition to the preparation of β-phase antimonene, α-phase antimonene has also been experimentally prepared. T Märkl et al. [52] grew 2 ML α-phase antimonene on an α-Bi topological insulator. Under the condition of ultra-high pressure, 2 ML Bi and Sb were sequentially deposited on molybdenum disulfide substrate to prepare antimonene. The substrate temperature was 295 K. The prepared antimonene was measured by STM and its period was calculated to be $7.3 \text{ nm} \pm 0.6 \text{ nm}$. The nontrivial topological structure of α-phase antimonene, belonging to the quantum spin Hall class, was studied.

2.4.2. Preparation of Single-Layer Antimonene

In 2016, Lei et al. [53] first reported the preparation of single-layer antimonene on Bi_2Te_3 and Sb_2Te_3 substrates with lattice mismatch of 1.9% and 0.8%, respectively, by molecular beam epitaxy. Subsequently, the preparation of single-layer antimonene on Bi_2Se_3 , PdTe_2 , Ge, Ag and Cu substrates has been reported by Lei et al., who deposited Sb on the substrate at room temperature and precisely controlled its growth rate. In order to study the chemical environment of Sb film, XPS (X-ray photoelectron Spectroscopy) measurements were conducted before and after the deposition of antimony on Sb_2Te_3 and Bi_2Te_3 substrates. The results show that Sb film is not coupled with the substrate, and the binding energy of Sb film in Sb/ Bi_2Te_3 is less than 0.09 eV compared with Sb/ Sb_2Te_3 . It has a relatively weak van der Waals force or relatively small charge transfer. The electronic structure of antimonene was measured by ARPES (Angle resolved photoemission spectroscopy). The results show that lattice distortion and charge transfer effect lead to the change in surface state band dispersion. The results show that the antimonene prepared by the method has high crystallinity, but its area is small. In 2018, Flammini et al. [54] prepared antimonene on Bi_2Se_3 substrate and grew antimonene films at room temperature by controlling the rate of 0.53 Å/min in a temperature-controlled Knudsen cell. The deposition of 0.15 ML (ML denoted as single-layer antimonene) and 2 ML of antimony on the substrate was observed with STM. Islands formed at a lower coverage and they reached coalescence at slightly higher than 2 ML. STM test showed that the coverage rate of antimonene was low, the uniformity was poor and the film size was small. At the same time, STM showed the existence of honeycomb surface structure of antimonene.

PdTe_2 was selected as the substrate for the epitaxy growth of antimonene for the following reasons: its lattice mismatch with the substrate is only 0.4%, and it has a chemically stable surface. Compared with the absence of lattice mismatch, the compressive strain will make the film grow prematurely from nucleation into the transition zone, while the tensile strain is the opposite. When the lattice mismatch is too large, the film will be subjected to a large stress, which may tear the film and transform the two-dimensional growth into three-dimensional growth. Wu et al. [55] prepared single-layer antimonene on PdTe_2 substrate. At the same time, the first-principles calculation was carried out based on density functional theory (DFT), and the experimental results were clarified. In an ultra-high vacuum (UHV) chamber with a pressure of 2×10^{-10} mbar, antimony atoms were vaporized in the Knudsen cells and deposited on a PdTe_2 substrate at a substrate temperature of 400 K, as described in Figure 9a. STM, LEED and XPS were used to characterise the film. As shown in Figure 9b, there are only six diffraction spots in this LEED pattern. These diffraction spots come from the lattice of antimony thin film and PdTe_2 substrate, indicating that antimony has a lattice almost consistent with the surface of PdTe_2 , and the adsorption layer of antimony is an ordered lattice. As shown in STM Figure 9b, the antimony atomic layer on the surface of PdTe_2 is smooth and homogeneous with no obvious defects. The height of the atomic layer is 2.8 Å, as shown in Figure 9e. Figure 9c shows a high-resolution STM image of single-layer antimonene, which is a graphene-like honeycomb lattice. Figure 9f shows the height profile of the flexed honeycomb lattice along the blue line in Figure 9c, which indicates that the periodicity of the graphene-like honeycomb lattice is 4.13 ± 0.02 Å. XPS measurements were used to study the interaction between antimonene and substrate. X-ray photoelectron spectroscopy measurements were obtained before and after the formation of single-layer antimonene. The results showed that the chemical state of the substrate did not change significantly and there was no chemical interface coupling between antimonene and substrate, that is, the interaction between antimonene and PdTe_2 substrate was very weak. It is also proved that antimonene is stable in air and the morphology and configuration of epitaxial single-layer antimonene are revealed for the first time at atomic scale. That is, single-layer antimonene has high chemical inertness and large band gap, which is a significant advance for electron and optoelectronics technology.

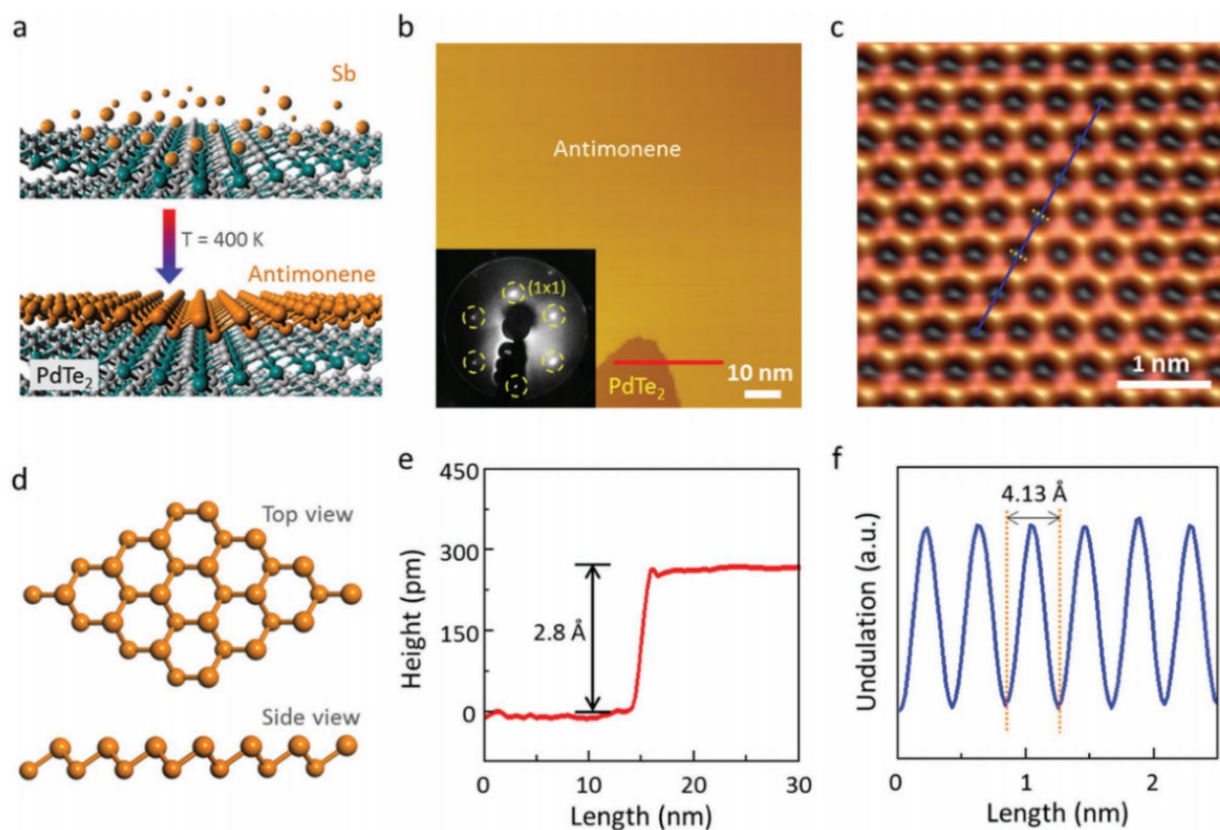


Figure 9. Antimonene formed on PdTe₂ substrate: (a) Schematic diagram of fabrication; (b) STM topographic map, illustration: LEED pattern of antimonene on PdTe₂. The six diffraction spots are due to the (1 × 1) structure of antimonene relative to the substrate; (c) Single-layer antimonene with atomic resolution STM image, showing graphene-like honeycomb; (d) Top view (upper) and side view (lower) of the structure of antimony honeycomb belt buckle; (e) The height profile along the middle red line (b) shows that the apparent height of the antimonene island is 2.8 Å; (f) Line profile corresponding to the blue line in (c), revealing periodicity of the antimony lattice (4.13 ± 0.02 Å). Reprinted with permission from Ref. [55]. Copyright 2016, John Wiley and Sons.

In addition to single-layer antimonene on compound substrates, antimonene was also prepared on pure metal substrates such as Ge and Ag. Matthieu et al. [12] synthesized monolayer and multilayer high quality antimonenes on Ge substrate with only 0.6% lattice mismatch with antimonene and studied the growth parameters. Knudsen cell was used to vaporize antimony crystals at an evaporation rate of 2–700 Å/min. The temperature of germanium substrate varied between room temperature and 330 °C, and the deposition rate and substrate temperature were controlled to obtain the growth parameters of antimonene. The crystal structure of antimony was found when the growth temperature was greater than 200 °C, as shown in Figure 10a. When the temperature is higher, it is determined that the island presents a more regular shape, as shown in Figure 10c–d. Meanwhile, it is proposed that the high temperature of the substrate will reduce the adhesion coefficient of Sb₄, hindering the nucleation and growth. By keeping the temperature constant and changing the deposition rate, it is determined that when the deposition rate is lower than 50 Å/min, 3D cone core is formed first, and then 2D growth occurs around it, thus forming a 3-fold symmetrical clover-like island (Figure 10c). When the deposition rate is 200 Å/min, 2D island and 3D island are formed. The growth model of antimonene with high nucleation rate and low growth rate is proposed. The growth dynamics were studied in real time by LEEM and LEED. In addition, STEM (scanning transmission electron microscopy) observations were combined with DFT calculations to study and discuss the Ge–Sb interface, showing that Sb–Ge covalent bonds do not exist. The flexion honeycomb

structure of β -2D antimony was measured by in STM and single-layer antimonene was characterized by high crystal quality and uniformity. Finally, the environmental stability of 2D antimony was determined by Raman spectroscopy and XPEEM (X-ray photoemission electron microscopy). The growth parameters of antimonene were investigated.

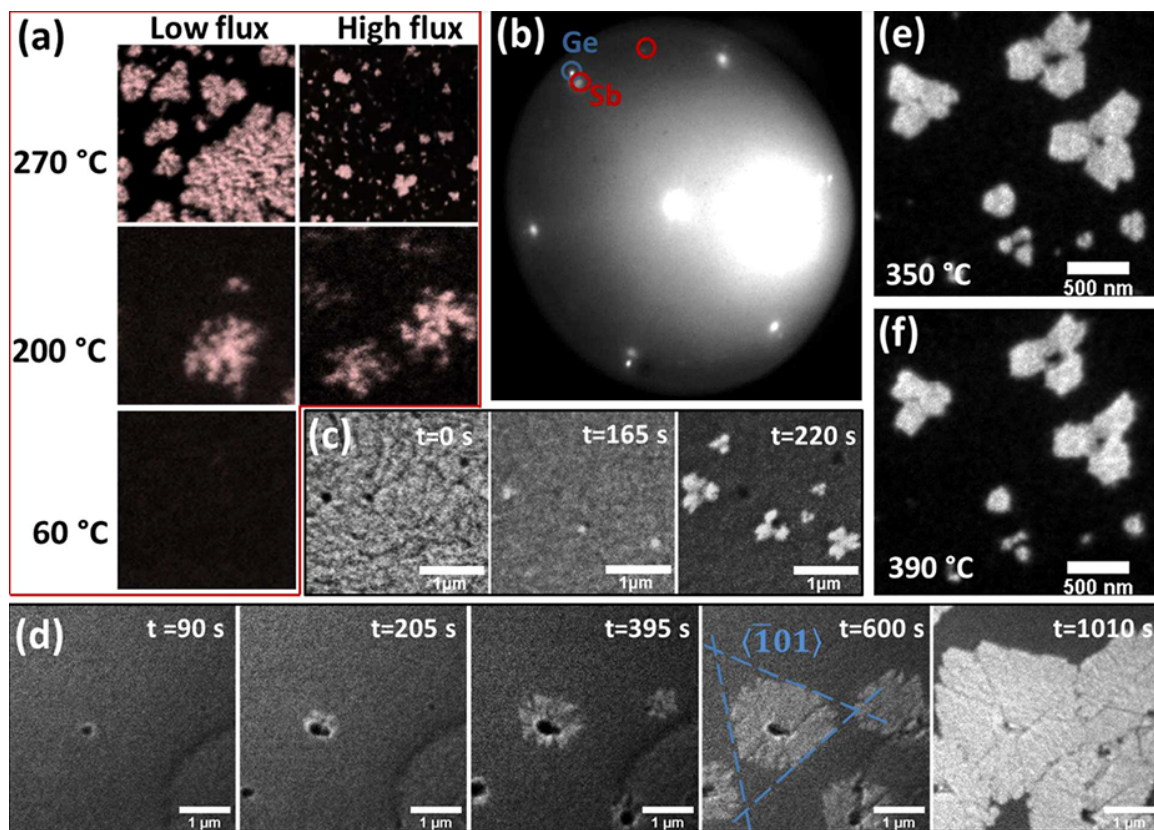


Figure 10. In situ LEEM/LEED observation of 2D Sb growth: (a) Effects of temperature and deposition rate on 2D Sb growth. In the low-flux zone, the deposition rates for each substrate temperature were $F(T = 60\text{ }^{\circ}\text{C}) = 2\text{ }\text{\AA}/\text{min}$, $F(T = 200\text{ }^{\circ}\text{C}) = 2\text{ }\text{\AA}/\text{min}$, and $F(T = 270\text{ }^{\circ}\text{C}) = 50\text{ }\text{\AA}/\text{min}$. In the high flux area, the deposition rate is $F(T = 200\text{ }^{\circ}\text{C}) = 10\text{ }\text{\AA}/\text{min}$, $F(T = 270\text{ }^{\circ}\text{C}) = 200\text{ }\text{\AA}/\text{min}$; (b) Typical post-growth LEED pattern (16 eV), showing Sb (red) and Ge (blue) spots; (c,d) 2D Sb growth snapshot; (c) = 280 °C, $F = 50\text{ }\text{\AA}/\text{min}$ and; (d) $T = 325\text{ }^{\circ}\text{C}$, $F = 200\text{ }\text{\AA}/\text{min}$; (e,f) signs of thermal decomposition. Reprinted with permission from Ref. [12]. Copyright 2017, American Chemical Society.

In order to study the properties of the tensile strain of antimonene, antimonene can be prepared on the substrate with large lattice mismatches such as Cu and Ag. Niu et al. [16] prepared antimonene on Cu(111) and Cu(110) substrates and compared the differences of antimonene prepared on different crystal planes. Single-layer antimonene was synthesized by evaporation at 450 °C, deposition at room temperature under ultra-high vacuum, and annealing at 700 K. The lattice constant of antimonene synthesized on Cu(111) substrate is 4.45 Å, while that of synthesized on Cu(110) substrate is 3.9 Å. It is shown that the epitaxial growth of antimonene on different crystal faces on the same substrate can regulate the electronic properties of the film by the strain and stress induced by the substrate, and can regenerate antimonene from antimony–copper alloy. The hexagonal lattice of antimonene was detected by STM, but the defect density was high. Antimony–copper band gap was measured with STS, and its stability was studied by X-ray photoelectron spectroscopy. In the same year, they also prepared single-layer antimonene on $\text{Cu}_3\text{O}_2/\text{Cu}$ substrate [56]. By evaporating Sb atoms, antimony was deposited at room temperature at a deposition rate of less than 0.1 mL/min and annealed at 550 K for 20 min.

Mao et al. [17] synthesized antimonene with curved structure on Ag(111) substrate. Ag(111) substrate was first cleaned during Ar ion sputtering for 15 min, and then annealed at 780 K in growth chamber for 40 min. During the preparation process, the substrate temperature was kept at 375 K, and then annealed at 550 K for 60 min. Sb–Ag alloy was formed on the silver substrate, and then the curved honeycomb structure of antimonene was stably grown on the top of the surface of AgSb₂. The lattice constant of the epitaxial antimonene on the substrate is 5 Å, which is greater than that of bulk Sb. It has been proved by experiments that antimonene epitaxial growth on the substrate with large lattice mismatch can achieve more than 20% tensile strain. What is more, antimonene at high tensile strain is particularly interesting because of its strong spin–orbit coupling effect. Since the bending degree of antimonene will have different effects on its corresponding electronic structure, Sun et al. [57] studied the preparation of single-layer antimonene with three high bending on Ag(111) substrate in 2020. Firstly, by coating the surface of Ag(111) with Sb–Ag, the Sb crystal was evaporated at 320 °C onto the surface of Ag at 80 °C with deposition rate of 0.01 ML/min. STM images show that the antimony flocculation is disordered. During the secondary growth of Sb atoms, the disordered antimony clusters previously nucleated can further develop and form a triangular antimony island. During the subsequent growth of Sb atoms, the previously formed Sb_xAg_{1–x} alloy is gradually transformed into an ordered SbAg₂ alloy, and then the antimony with curved surface is formed on the surface of the alloy. The STM image resolves the atomic structure. Compared with Mao et al.’s preparation of antimonene on silver substrate, this one has a different bending structure. It can be seen that the preparation of antimonene on the same substrate under different conditions will produce different electronic structures.

In 2020, Shi et al. [19] prepared single-layer antimonene with α -phase with thickness of 6.8 Å on SnSe substrate. High-quality antimony was evaporated from standard Knudsen cell with pressure of 1×10^{-10} mbar and beam source of 0.3 ML/min to prepare antimonene. At the same time, the difference of electronic structure on MoTe₂ substrate shows that different electronic structures will be caused by inconsistent electron transfer between different substrates. It proves that interface engineering can be used to adjust the interfacial charge transfer, so as to adjust the electronic structure of epitaxial monolayer. The morphologies of substrate and antimonene were detected by in situ monitoring of RHEED (reflection high-energy electron diffraction) patterns. The streaks of exposed SnSe indicated that it had high crystal quality and an atomically flat surface, and the streaks of antimony film indicated that Sb was grown layer by layer on SnSe. STM images showed high quality single-layer antimonene without obvious defects. The electronic structure was measured with STS, revealing band gap changes between 1, 2, and 3 ML layers. dI/dV spectra on both double and triple layers of antimonene showed the density of metallic states, indicating that the semiconductor–semimetallic crossing occurred at 2 ML. Lu et al. [58] also prepared α -phase antimonene with a thickness of 6.5 Å on SnSe. The protection of asymmetric α -phase antimonene against Dirac state was also studied. The anisotropy of antimonene with Dirac fermion states and Dirac states at high symmetric momentum points has been studied by Angle resolution spectroscopy and first principles. Compared with the spin-free Dirac state of graphene, spin–orbit coupling exists in the Dirac state of α -phase.

As described in Table 1, antimonene has been successfully prepared on substrates of compounds such as Bi₂Te₃, Sb₂Te₃ or PdTe₂, on substrates such as pure metal Ge, Ag and Cu, or on two-dimensional substrates. The antimonene generated on the substrate with small lattice mismatches such as Bi₂Te₃, Sb₂Te₃, PdTe₂ or Ge has a weak interaction with the substrate. The hexagonal honeycomb structure of antimonene with curved structure was prepared on the substrate with large lattice mismatch such as silver and copper. The antimonene was formed into alloy, and then further growth continued. The tension strain of the substrate could be higher than 20%, and the band gap of antimonene could be changed by this method. On graphene, MoS₂ and other two-dimensional substrates, due to its hexagonal structure similar to antimonene and the van der Waals force between them, antimonene can be grown on such substrates, and it is easy to generate continuous

antimonene films. Because of the different charge transfer on different substrates, the electronic structure of antimonene will also be affected differently. For example, in different crystal faces of copper, the lattice constants of single-layer antimonene is not the same, and different substrates will lead to different tensile strains [16]. In addition to the influence of the substrate, the substrate temperature will also affect the adhesion of antimony; generally speaking, the higher the temperature of the substrate, the better the adhesion, but at the temperature above 300 °C, the adhesion will decline. At the same time, the rate of the beam source also has an effect on the preparation of antimonene. For example, when preparing antimonene on germanium substrate, Matthieu et al. [12] proposed that the nucleation of the beam source at a high speed is conducive to the nucleation of 2D hexagonal island, while the growth of the beam source at a low speed can grow islands with a large area. Researchers generally use STM, AFM, LEED to study the morphology of antimonene, such as its honeycomb surface structure, size, etc. The interaction and chemical stability between antimonene and substrate were studied by XPS and XRD, while STS was used to study the band gap and electronic structure of antimonene. Compared with other methods for the preparation of antimonene, molecular beam epitaxy can control the thickness the atomic level, that is, it can optimize the experimental conditions by precisely controlling the experimental parameters and observing the growth process in real time, and prepare single-layer antimonene. Compared with the mechanical exfoliation method, it has a high repeatability rate, and compared with the liquid exfoliation method, contamination from the solvents can be avoided, but its equipment is too expensive.

Table 1. Conditions of epitaxial preparation of antimonene.

Thickness	Mean Transverse Dimension	Substrates	Antimony Source Temperature (Molecule)	Growth Temperature	Deposition Rate	References
1–50 nm	5–10 µm	mica	660 °C	380 °C	—	[4]
1–5 BL	10–20 nm	Bi ₂ Te ₂ Se	—	room temperature	—	[39]
17 nm	16.2 nm	MoS ₂ /Sapphire	500 °C	200 °C	—	[5]
4–9 nm	1–3 µm	Graphene/Ge	Sb ₄	—	16 nm/min	[40]
single-layer	—	Bi ₂ Te ₃ , Sb ₂ Te ₃	—	room temperature	—	[41]
single-layer	—	Bi ₂ Se ₃	—	room temperature	0.53 Å/min	[42]
single-layer	20 nm	PdTe ₂	—	127 °C	—	[43]
single-layer	—	Ge	Sb ₄	room temperature–330 °C	2–700 Å/min	[7]
single-layer	—	Cu(111), Cu(110)	450 °C	room temperature	—	[11]
single-layer	—	Ag(111)	—	102 °C	—	[12]
single-layer	—	Ag(111)	320 °C	80 °C	0.01 ML/min	[45]
1–3 ML	—	SnSe	—	—	0.3 ML/min	[14]

2.5. Other Methods

In 2017, Lu et al. [59] synthesized antimonene with an average thickness of 31.6 nm and a quantum dot with an average transverse size of 3.4 nm based on electrochemical exfoliation and sonochemistry methods, and further studied the corresponding nonlinear optical response at visible wavelengths for the first time. The results show that antimonene has a large nonlinear refractive index of $10^{-5} \text{ cm}^2 \cdot \text{W}^{-1}$, and has high stability under ambient condition.

In 2020, Marzo et al. [60] synthesized antimonene with multilayer thickness and micrometer size by electrochemical spallation in the electrolyte Na₂SO₄ and Li₂SO₄, proving

that the type of electrolyte and the change in voltage polarity will affect the surface oxidation degree and thickness of the nanosheet.

In 2020, Zhang Y et al. [61] obtained microcrystalline antimony by ball milling bulk antimony, and then synthesized antimonene with a thickness of approximately 7 nm through solvothermal reaction with ethylenediamine (EDA). In order to achieve the deposition of platinum on antimonene nanosheets, platinum salt was directly introduced into the exfoliation solution of antimony microcrystals and EDA. Since EDA is a reducing agent, Platinum atoms were reduced and deposited on the surface of antimonene nanosheets to be used as the carrier of platinum catalyst for formic acid fuel cells.

In the same year, Wu et al. [25] prepared antimonene nanosheets with a thickness of 4–32 nm and an average size of several hundred nm by laser irradiation of antimony powder in isopropyl alcohol. As shown in Figure 11, the mixture of isopropyl alcohol and antimony was irradiated by a pulsed laser. Under the laser irradiation, the surface of the material absorbs laser photons and produces a stream of high-temperature and high-pressure plasma that breaks down the van der Waals bonds in the antimony layer and rearranges to form nanosheets. After 30 min of laser irradiation, the suspension was obtained and ultrasonic treatment was performed for 10 min. The suspension was then centrifuged at 4000 rpm for 15 min. At the same time, the nonlinear characteristics of the prepared antimonene nanosheets were tested, as shown in Figure 11. When the laser energy irradiation is weak, the absorption of single photon is displayed, and when the laser energy is high, the absorption of two-photon is dominant. The FON (the lower the FON, the better the FON) of 0.162 J/cm^2 is lower than that of carbon nanotubes (2.07 J/cm^2) [62], indicating that antimonene has great potential in laser protection.

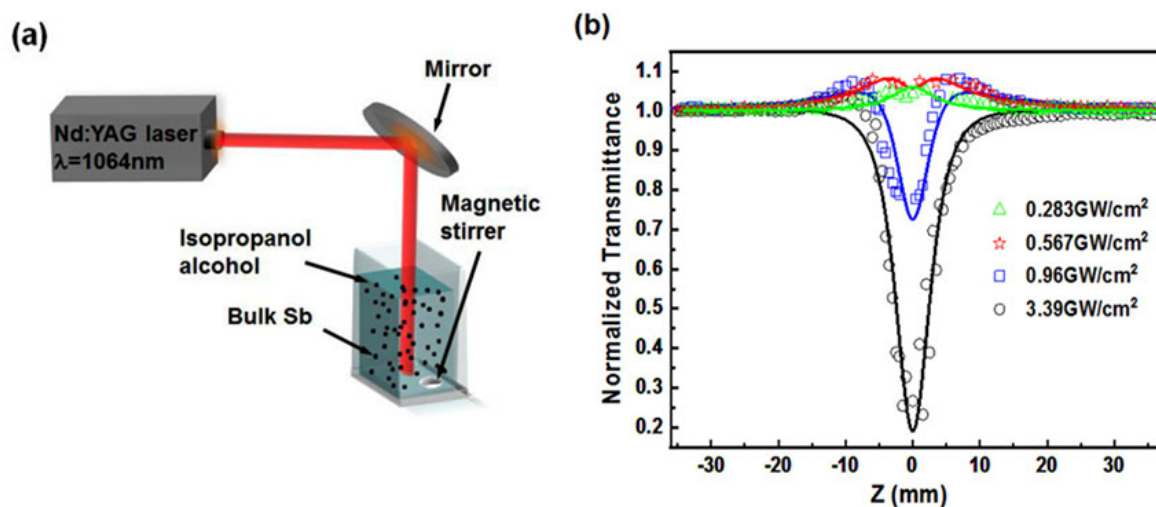


Figure 11. (a) Schematic diagram of laser irradiation; (b) The results of the open-hole Z-scan experiment. Reprinted with permission from Ref. [25]. Copyright 2020, American Institute of Physics.

3. Practical Applications

3.1. In Composite Materials

The doping of antimonene nanosheets in the graphene-based composite sponge promotes the electrolyte interactions at the interface due to the high surface area of the antimonene layered structure. When the antimonene is distributed on the surface or inside the matrix, it can ensure the free movement of carriers, thereby improving the overall electrochemical performance and sensitivity of the material by 44%, while maintaining the conductivity of the material. Yu et al. [11] prepared antimonene/graphene composite sponges with regular pore structure of melamine sponge as substrate. The crucible containing the graphene intercalation compound was heated to 700°C for 3–4 min. After cooling, the graphene sheets were then placed in acetone for ultrasonic treatment. The graphene films were then dried at 25°C for 3–4 h. The antimonene solution was obtained by grinding,

adding deionized water and ED-2003 solution for ultrasonic and centrifugal treatments. Then, the modified graphene sheet and antimonene solution were mixed by solution blending method, and attached to the sponge bone evenly. Then, PVA/KOH gel was installed between the two sponge electrodes as electrolyte and separator. The antimonene/graphene composite sponge is used as a supercapacitor and capacitor sensor. During the preparation of the capacitive sensor, conductive carbon cloth and solid electrolyte were introduced to assemble the flexible wearable sensor. The resulting pressure sensor has good sensitivity, high flexibility and high mechanical, temperature and sensing stability. The pressure sensor has been successfully applied to the supercapacitor and human motion monitor. In order to achieve the integration goal, the functional devices are connected to the sensor and the supercapacitor, as shown in Figure 12a,b. When the mechanical pressure is applied, the sensor is compressed, resulting in a sharp increase in the current. The sensors are mounted on the fingers and wrists, and when pressure is applied to the fingers, they show an electric current to detect movement signals such as distortion of the fingers and wrists.

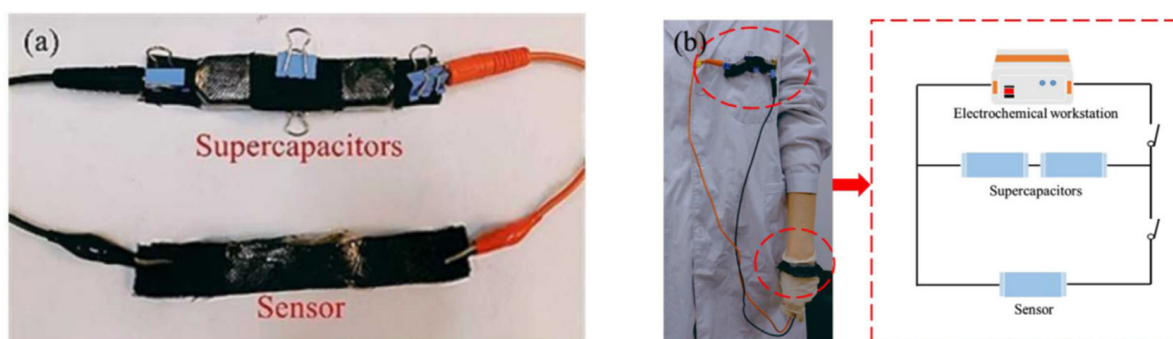


Figure 12. (a) Schematic diagram of the sensor system; (b) The flexible sensing system includes a supercapacitor placed on the surface of the coating and a sensor attached to the skin, as well as a schematic diagram of the complete circuit. Reprinted with permission from Ref. [11]. Copyright 2022, Elsevier.

Chen et al. [63] also calculated the electronic and optical properties of the composite germanene and antimonene nanosheets theoretically. Ge/Sb bilayer is constructed, and it is determined that the d orbitals of Ge and Sb almost overlap in the whole energy range, indicating that their monolayers can be combined with each other through orbital hybridization, resulting in strong bonding strength. In addition, the introduction of external electric field can also adjust the band gap, and its structural work function is calculated to be 4.49 eV. This composite material has application potential in field reflection devices.

3.2. Energy Storage

Antimonene, with a theoretical capacity of up to 660 mAh g^{-1} and a large surface area of active material, is an excellent choice as a cathode material for batteries. Based on the results of X-ray diffraction (XRD), selected area electron diffraction (SAED) and density functional theory (DFT), the superior sodium storage properties of the few layers of antimonene were determined and the mechanism of sodium conversion/removal of the few layers of antimonene was elucidated [64]. Several layers of antimonene underwent reversible crystal phase evolution ($\text{Sb} \rightleftharpoons \text{NaSb} \rightleftharpoons \text{Na}_3\text{Sb}$) and Na ion alloy reaction along the a/b axis, resulting in in-plane anisotropic lattice expansion, while due to unconstrained in-plane expansion along the a/b axis, few-layer antimonene can realize sodium ion storage with high structural stability. Meanwhile, it is determined that the Na^+ diffusion potential of antimonene is only 0.14 eV, which is lower than that of other two-dimensional materials.

In this study, antimonene was used as the working electrode and sodium as the counter electrode. Due to the large surface area of electrolyte/electrode in the first cycle process, the excess side reactions resulted in irreversible effects. The low-layer antimonene anode

provides a capacity of 642 mAh g^{-1} at 0.1 C . When the current density increases to 5 C , the capacity is only 429 mAh g^{-1} . When the current density returns to 0.1 C after 36 cycles, the capacity also returns to 642 mAh g^{-1} , which shows that it has good reversibility. The long-term cycle of antimony and antimonene was measured as shown in Figure 13a at a current density of 0.5 C , and the stable capacity of 620 mAh g^{-1} was obtained at 0.5 C . For antimony, the capacity of bulk Sb rapidly decays due to significant volume changes during sodium conversion and removal, resulting in severe pulverization. However, the Sb atom content of antimonene is 93.9% after 150 cycles, and the Coulombic efficiency is close to 100%, as shown in Figure 13b. They are the highest capacity and Sb utilization reported so far.

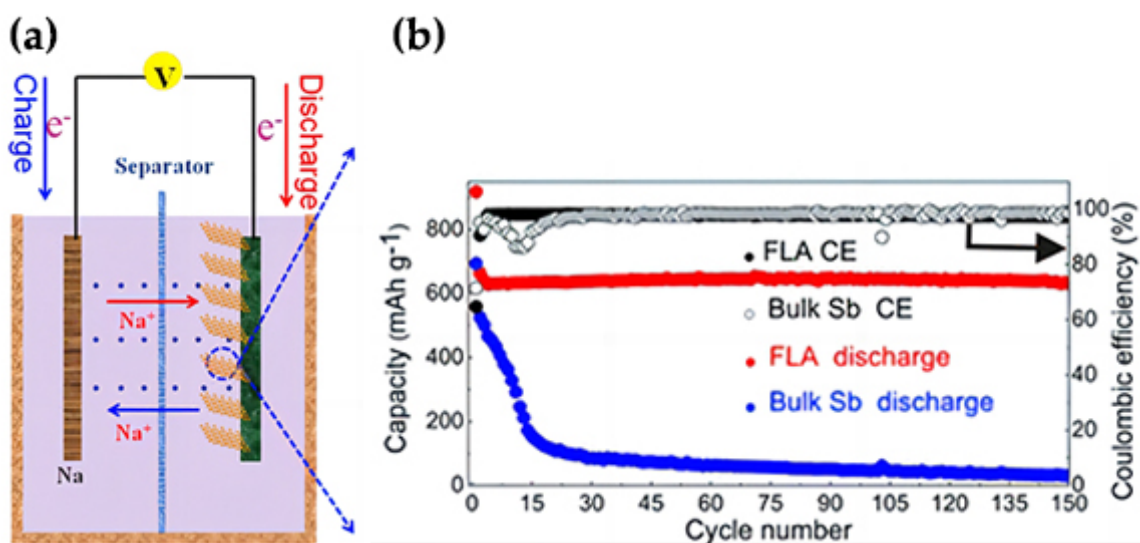


Figure 13. (a) Schematic diagram of the Na-ion half-cell composed of few-layer antimonene; (b) Long-term cycling performance and Coulombic efficiency of few-layer antimonene and bulk Sb powder at a rate of 0.5 C . Reprinted with permission from Ref. [64]. Copyright 2018, American Chemical Society.

Layered two-dimensional (2D) materials are ideal materials for high-performance lithium-ion battery electrodes due to their high surface-volume ratio, which can alleviate the strain caused by volume changes during lithium absorption and release. However, the van der Waals force limits the motion of lithium atoms and thus reduces the efficiency of the battery. To solve this problem, charge transport has been improved by creating ordered holes in two-dimensional sheets. However, the complexity of the process limits the practical application, and single-layer antimonene allows the movement of lithium atoms without structural engineering conditions. Kistanov et al. [65] proved the theory through the first-principle study, and found that lithium atoms have an ultra-low diffusion barrier (0.36 eV) on antimonene, which is consistent with the movement of lithium atoms in the horizontal plane. The results show that antimonene is a two-dimensional material with rapid outward diffusion of lithium, which may be unique in the design of a new generation of lithium-ion battery materials and solid ion conductors.

Zhang et al. [66] applied antimonene quantum dots as photoactive materials in solar cells. Based on the application of antimonene quantum dots as sensitizers in solar cells, the photoelectric conversion efficiency of antimonene quantum dots remains above 90% of the initial value after 1000 h. Meanwhile, antimonene quantum dots showed excellent photostability against oxidation and degradation, indicating that antimonene is indeed a promising optical material for solid solar cells.

3.3. Cancer Therapy

Due to the high specific surface area and good photothermal effect, antimonene quantum dots show good ability of drug delivery or photothermal therapy (converting light energy into heat energy under light irradiation can induce the thermal ablation of cancer cells, thus killing malignant tumors) in the field of cancer therapy.

Duo et al. [67] proposed ultra-thin antimonene nanoparticles as a novel radiosensitizing agent that achieves effective chemoradiotherapy effects by inducing a strong oxidative stress response and significant *in vivo* radiotoxicity.

The practical use of metal radiosensitizers is hampered by a number of practical limitations. First, some nanoparticles with low clearance rates, such as silver nanoparticles, can cause neurotoxicity, genotoxicity or cellular dysfunction *in vivo*. Second, the manufacture of multifunctional therapeutic radiosensitizers always requires the addition of materials in multiple steps, leading to unpredictable safety issues *in vivo*, such as undefined biotransformations. Antimonene quantum dots and nanoparticles were prepared using ethanol as solvent by conventional liquid-phase separation method, and PLGA (lactic co-glycolic acid) was prepared by emulsifying solvent of oil in water to be used as the carrier of antimonene quantum dots and nanoparticles. The carrier improves the dispersibility of antimonene quantum dots in physiological environment and the stability of antimonene nanosheets. While antimonene quantum dots and antimonene nanosheets can be oxidized to Sb_2O_3 by X-ray as shown in Figure 14a, Sb_2O_3 produces ROS with specific cytotoxicity to cancer cells as shown in Figure 14b. Under X-ray irradiation, AMQD and AMNSs with more surface defects promote electron transfer, produce ROS and mitochondrial rupture in cancer cells, and inhibit tumor formation through hypoxia regulation. The excellent absorption of the antimonene material in the near infrared region (808 nm) makes itself an ideal photoacoustic (PA) reagent for the detection of deep tumors.

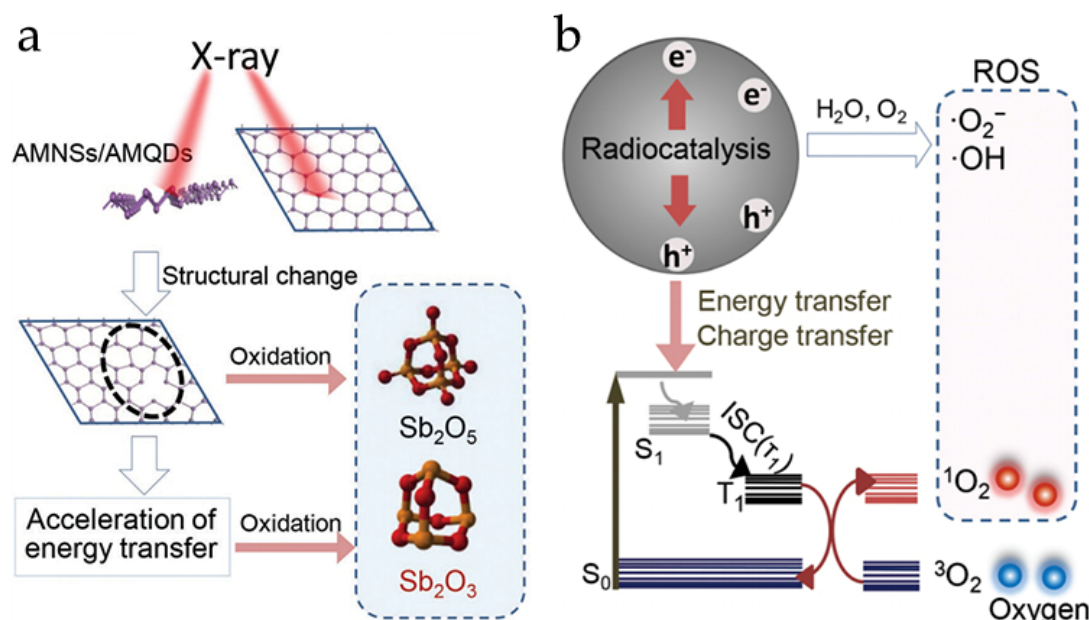


Figure 14. Mechanism of antimonene in the treatment of cancer. Reprinted with permission from Ref. [67]. Copyright 2019, John Wiley and Sons.

In addition, antimonene [68] can also be used as a contrast agent to monitor somatic cells and image tumors *in vivo*. In the near infrared window of 800 nm, the molar extinction coefficient of antimonene nanoplate is 2.24×10^9 , which is higher than that of other small molecules. The results show that antimonene nanosheets are excretable and biocompatible in nude mice, that is, antimonene nanosheets can be used as an excellent photoacoustic contrast agent.

3.4. Nonlinear Optics

Yuan et al. [27] applied antimonene to Erbium-doped fiber lasers with a cavity length of 9.5 m through the sandwich structure, and obtained passive Q-switched signals by adjusting the polarization state of the laser cavity. The diagram of laser cavity connection is shown in Figure 15. The antimonene nanosheet was used as the experimental material to verify the relatively stable absorbance at approximately 1.5 μm . The pump with the wavelength of 976 nm and the maximum output power of 600 mW was connected to the wavelength division multiplexer at 980/1550 nm. The Erbium-doped fiber was used as the gain medium, the polarization isolator was used as the guarantee of one-way transmission of the optical path, and the PC was used to change the polarization state. The nonlinear results based on the antimonene saturation absorber (Sb SA) show that the saturation strength of the saturation absorption test is 1.52 MW/cm² and the modulation depth is 11.63%. At 1558 nm, a stable signal output is obtained, which does not change significantly for a long period of time. The signal-to-noise ratio (SNR) of the output signal is ~48 dB, which effectively proves the feasibility of antimonene and its great application potential in fiber lasers.

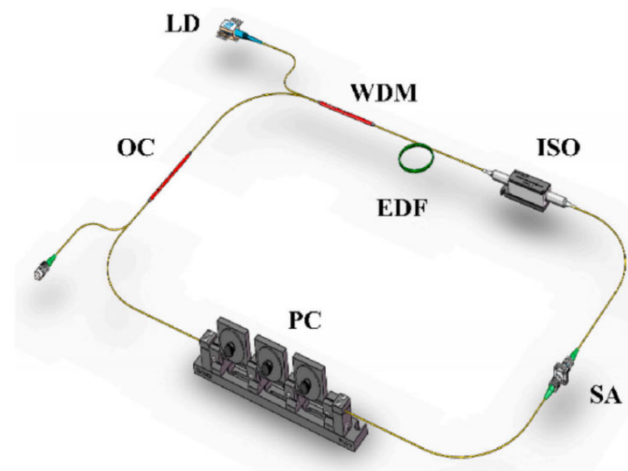


Figure 15. Schematic diagram of laser cavity connection. Reprinted with permission from Ref. [27]. Copyright 2021, Optical Materials.

With the increase in the output power of the pump source, the repetition frequency range of the fiber laser is from 25.60 kHz to 124.1 kHz, and the duration of the Q-switched pulse is reduced from 5.10 μs to 1.42 μs . The minimum pulse duration after Gaussian fitting is 1.42 μs . Meanwhile, the saturable absorbers formed by different materials are compared, as shown in Table 2. It can be seen from the figure that antimonene has higher output power and shorter pulse duration, which proves that antimonene has great application advantages in laser Q-switching.

Table 2. Comparison of applied power and pulse time of various materials in laser [27].

Materials	Wavelength (nm)	Output Power (mW)	Pulse Duration (μs)	Pulse Energy (nJ)
Graphene	1539.6	3.38	3.89	28.7
BP	1562.87	1.5	13.2	94.3
Silicene	1567.1	0.89	2.32	–
TiO ₂	1558	~0.26	1.84	~2.3
ZnO	1550	1.2	1.68	46
WSe ₂	1560	1.23	3.976	17
MoS ₂	1068.2	0.46	2.2	6.9
Antimonene	1559.63	2.85	1.58	37.9
Antimonene	1558	4.73	1.42	54

Luo et al. [69] proved that antimonene can be used as a saturable absorber in mid-infrared spectrum. They prepared multilayer antimonene by liquid phase separation method and coated it on a gold mirror, using it as a reflective saturable absorption device. At the wavelength of 2865 nm, the pulse energy is 0.72 μJ , the maximum output power is 112.3 mW, and the shortest pulse time is 1.74 μm . The maximum repetition frequency is 156.2 kHz.

Using antimonene as an all-optical modulator, Wang et al. [70] designed an active Q-switched laser with all-optical modulation. Suspension droplets of antimonene prepared by liquid phase separation were put into self-made microfibers. It was found that antimonene has a wide band response and a wide spectrum response range. The all-optical modulator is applied to a Q-switched laser, and the repetition rate of the pulse train is changed from 0.96 kHz to 6.64 kHz by changing the pump pulse duty cycle.

4. Conclusions

Antimonene has the characteristics of high carrier mobility, adjustable band gap, saturable absorption and high stability. In order to explore the practical applications of antimonene, extensive research has been conducted on its synthesis. Mechanical exfoliation method has the advantages of simple production process and low cost, can be used to prepare single or few-layer antimonenes with good film stability, but because the adhesive tape will take away a large number of thin sheets, the peeling efficiency is low, and it is not easy to control the level. Compared with the mechanical exfoliation method, the liquid phase exfoliation method has a higher yield. The liquid phase exfoliation method has the advantages of low cost, simple process and relatively large yield of the film, but it is affected by solvents, ultrasonic cleaning process and so on. Due to the influence of residual solvent and capillary and adhesion force, the film thickness detection is not accurate, and therefore the quality of antimonene will be affected. The size of single-layer antimonene prepared by this method is generally larger than that of the mechanical exfoliation method. Molecular beam epitaxy has better repeatability, and its resulting film crystallization is perfect, its substrate temperature, the growth rate of the film, the composition and doping concentrations can be adjusted as required, but the growth rate is relatively low and the equipment facility is expensive. With this method, the size of single-layer antimonene is mostly tens of nanometers, and the preparation process is also affected by many factors. Meanwhile, antimonene has some advantages in sensor, battery, medicine and laser applications.

The preparation of antimonene using MBE is affected by substrate, growth temperature, beam flux, etc. Si substrate is a particular candidate for MBE growth of antimonene, owing to several reasons. Compared with uncommon substrates such as PdTe_2 , Si is not only lattice-matched to the epitaxial material, but also has mature technology, low cost, and its pretreatment is less difficult. In addition, Si is the basis of CMOS process, which can bring great potential for practical applications of antimonene. When the substrate temperature is 90–130 $^{\circ}\text{C}$, the adhesion coefficient of antimony is moderate, and higher than at room temperature, which is conducive to antimonene thin film growth with good uniformity and large size. As a next step, we propose to control the substrate temperature to maintain it within 90–130 $^{\circ}\text{C}$, to look for the possibility of preparing monolayer antimonene by attempting the rapid nucleation and slow growth mode.

Antimonene films have the characteristics of large band gap, high photothermal efficiency, high carrier mobility and broadband nonlinear optical response, are suitable for optical switch, optical modulator, optical threshold device and other optoelectronic devices. Antimonene transistors, owing to its unique characteristics, have gradually become a research hotspot in the field of optoelectronic materials. Antimonene transistors are expected to replace silicon transistors in the near future.

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