FLEXIBLE ELECTRONICS USING 2D MATERIALS

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With the latest developments in technology, there has been an increased focus on the rise of flexible electronics. This coupled with the emergence of 2D materials has begun a new trend - "Flexible Electronics using 2D materials". Flexible electronics are already prevalent in today's industry so existing examples will be used as a benchmark to define the fundamental characteristics of flexible electronics. These will be based on Low-Density & 2D Flexibility, Robustness and Carrier Mobility. There are many types of 2D materials but for the purposes of this review, three have been explored- graphene, hexagonal boron nitride (hBN) and Xenes (silicene). The review will explore the existing applications of these 2D materials for flexible electronics and how they can be advanced. There are limitations to these materials, the main constraint is the manufacturing methods, of which Roll-to-Roll, Gravure and Inkjet printing will be talked about. If these limitations are overcome the future prospects of flexible electronics using 2D materials can be discussed.

Index Terms—flexible electronics, 2D materials, graphene, monolayer, TMD, xenes, roll-to-roll, Van der Waals.

I. INTRODUCTION

HROUGHOUT the last number of years, there have been numerous developments in the industry which has led to the production of curved and touch screens as well as the downsizing of everyday use electronics. This has made the popularity of flexible electronics skyrocket, this increasing demand also came with the emergence of 2D materials at a similar time frame, this has given an advancement to the field by merging these two fields to create its own specialised field which is flexible electronics using 2D materials. As there are already existing examples of flexible electronics within the industry, there can be a standard made using these examples. These standards will be the characteristics on which we will base the desired properties for flexible electronics using 2D materials, the desired properties will be low-density & 2D for the downsizing of electronics, Flexibility and Robustness for the use of flexible materials and Carrier mobility for the use of electronics [1].

The use of 2D materials allows for a unique set of physical, chemical, and mechanical properties previously achievable in the realm of 3-dimensional materials. Within this paper the focus will be on three specific 2D materials, these are graphene, hexagonal boron nitride and Xenes (silicene). there

will be high attention to the mechanical and electrical properties as the material needs to adhere to the desired properties of flexible electronics, but there will be a focus on other specific properties that make the material special. These 2D materials will be scrutinized for the existing applications they are already in use, things like OLED and flexible transparent conductors for touch screen applications to name a few [2].

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There will be limitations to these flexible electronics using 2D materials in the existing industry, to be more specific the limitation will be the production of said 2D materials so there will be discussions on more relevant manufacturing methods with the focus being on Roll-to-Roll, Gravure and Inkjet printing. Therefore, if this limitation can adhere then the future application for 2D materials can be extensive so there will be an exploration of future prospects of flexible electronics using the 2D materials that will be looked at.

When implemented in sensors, the detection limits of 2D materials far outrank their 3D predecessors. The compatibility of 2D materials within the assembly process is another desirable trait. This is because ultrathin nanosheets are lightweight, portable and, energy efficient when used in IoT applications [3]. There have been great demands for the research and application of flexible electronics in the previous decade, and with the development

of Industry 4.0, this trend is set to continue. Many sectors have opted to use flexible electronics in their work. Biomedical applications of 2D materials are in the area of wearable electronics for use in cardiac and respiratory monitoring [4] and in electroencephalograms (EEGs) for brain scans.

The Smart Technology sector has also observed the benefits of flexible electronics and has employed flexible screens for image or video display. This development is of great interest to marketing professionals who have chosen to use public spaces for advertising products by incorporating these screens onto park furniture. [5]

Flexible electronics have been studied within the automotive industry to assist in personalisation and identification coming in the year 2025. Flexible sensors are used to detect who is driving and automatically set preferences in the car such as seat position, speaker volume and driving mode. By implementing 2D materials to fabricate these flexible electronics, the scope for potential improvement to human life is vast. [5]

Previously unimaginable technologies will be made possible by combining the unique properties provided by 2D materials and the innovation of flexible electronics.

While there will be different characteristics and properties seen between the materials- the main point of interest of this report will be the branch that has properties related to flexible electronics.

The topics covered in this review will the fundamentals of flexible electronics, manufacture of flexible electronics, applications and future prospects. The final topic will be an analysis of current characteristics of flexible electronics so that we can use these properties as a guide for "Flexible Electronics using 2D Materials".

II. FUNDAMENTALS OF FLEXIBLE ELECTRONICS

The field of flexible electronics is the research of technology that allows circuits to be built to become bendable and stretchable. This allows for new product innovations that weren't at all possible with conventional electronics. Examples of 2D materials can be seen in Figure 1 To fully cover the terms of flexible electronics, they need to have the following characteristics:

• Low density and 2D – Allow the material to act like a sheet that can attach to other materials.

- **Flexibility** The ability to be conformally contacted to any type of rough surface without losing its effectiveness.
- **Robustness** The ability to withstand great amounts of stress considering the application size, this would mean it would have good tensile strength.
- Carrier mobility This is the measure of how fast the mobility of the charge carrier is through a given material. An example of this can be, how quick an electron can go through a semiconductor.

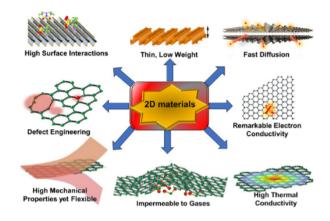


Fig. 1. Examples of 2D Materials [6]

There are many different applications to flexible electronics, but the limitation that these materials come to is their cost-effectiveness. There are many ways to create 2D materials with some being cost beneficial on an industrial scale, the most promising process being inkjet printing.

With the field being largely untapped, there is a lot of room for future innovation. While examples of current implementations can be seen in the likes of transparent conductors, touch screen displays and organic light-emitting diodes (OLEDs), etc., it is unknown how far its reach can stretch.

With these concurrent applications, there will need to be an exploration of candidate 2D materials which achieve the fundamental properties with a spotlight to carrier mobility.

III. CANDIDATES FOR MATERIALS

For use with electronics, one of the most important characteristics to observe is the carrier mobility within semiconductors. The three main candidates explored will be graphene, hexagonal boron nitride (HBN) and xenes (silicene).

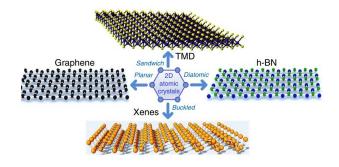


Fig. 2. Examples of atomic structures of 2D materials [7]

A. Graphene

Specifically, an sp²-bonded carbon hybrid will be covered. The model for this material consists of three sp² hybrid orbitals which are arranged at 120° to each other in one plane. These sp² orbitals are what make up the sides of the hexagonal shape of the lattice. The remaining p orbital is at right angles to these sp² orbitals and gives the material some unique characteristics as these p orbitals act like free-electron orbitals. Structures can be seen in Figure 2. [1]

The single-atom-thick material is reviewed as it contains some very noteworthy characteristics. The mechanical properties have a low density of 2g/cm³, Tensile strength 130 GPa, Young's modulus of 0.5–1TPa and Spring constant 1–5 N/m. Electrical properties of graphene also show great promise. High electrical conductivity helps in the use of graphene in electronics. This conductivity is caused by low defect density in the lattice of the crystals which act as a scatter site that can also hinder charge transportation through the decrease of the electron free path.

High electron mobility by using an ambipolar electric field. This is applying a required gate voltage that can adjust the charge carriers within the material. Through the use of a positive bias, the concentration of the holes in the balance bands can be enhanced. Through the use of a negative bias, we can enhance the concentration of the holes within the valence bands.

B. Diatomic Hexagonal Boron Nitride (h-BN)

The structure of Hexagonal Boron Nitride (h-BN) is the same as that of Graphene; hexagonal with Boron and Nitrogen atoms occupying the A and B positions held within the Bernal structure.

Hexagonal Boron Nitride is acquired by the method of CVD-growth. The strong in-plane bonds prevent free dangling bonds, which make the nanosheet chemically inert. When a larger TMD monolayer structure is generated, the hBN act as an ideal dielectric structure when layered with Graphene. The Dielectric properties of hBN result in ε -4 and a V Breakdown of 0.7 V/nm. h-BN also outperforms Silicone as an insulator with a bandgap of 5.97eV [6]. The structure can be seen in Figure 3.

The thermal conductivity of hBN is unrivalled when used in a TMD. The thermal conductivity of hBN is 600 times more efficient than silicon dioxide. Again, its solid in-plane bonds allow for excellent heat distribution, quickly spreading thermal energy out to heat sinks. The more hBN sheets present in a layer the more significant the thermal distribution. [8], [9]

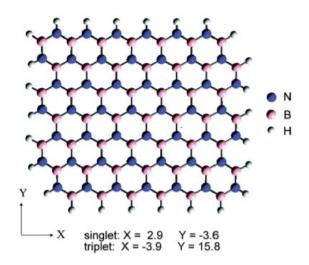


Fig. 3. Structure of hBN [10]

C. Monoatomic Buckled Crystals (Xenes)

Extensive attention has recently been given to the family of materials known as Xenes. This monoatomic group of materials consist of various different chemical elements but by definition, these materials only consist of one type of element and are a 2D allotrope of already known materials.

Most of the knowledge referring to this family of materials is limited due to research only beginning in 2011, with the synthesis and separation of monolayers of titanium carbide. This leads to limitations in a full understanding of its capabilities. Following the previous materials that have been covered xenes consists of metallic and semiconducting materials.

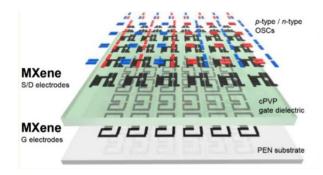


Fig. 4. Structures of Graphene and Silicene [11]

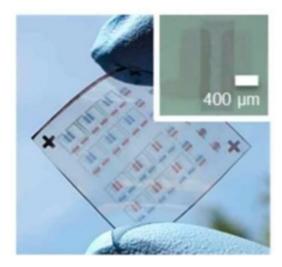


Fig. 5. Structures of Graphene and Silicene [11]

Monoatomic materials are by definition made of only one type of element. The composition of these materials is just a 2D allotrope of already well known and studied materials.

For clarity, this review will cover silicene. Studies into this particular field of 2D materials arose during 2012 when silicene was discovered [2]. Upon discovery, it was clear that silicene is to silicone, what graphene is to graphite, i.e. a two-dimensional 'slice' of silicone. Silicene would be an example of a semiconducting member of the wider Xenes family. Currently, the main method of producing silicene is using a method called epitaxial growth. There is a limitation to silicene as it cannot be pulled out of a stack that is made of tightly held together with 2D layers through loose bonding. Examples of which can be seen in Figures 4, 5.

1) Silicene

The mechanical properties of silicene are split into the armchair and zigzag directions. In the armchair direction the elastic modulus is 61.7 GPA.nm, Poisson's ratio is 0.29 and ultimate tensile strength is 7.2 MPa. In the zigzag direction, the elastic modulus is 59 GPA.nm, Poisson's ratio is 0.33 and ultimate tensile strength is 6.0 MPa [12].

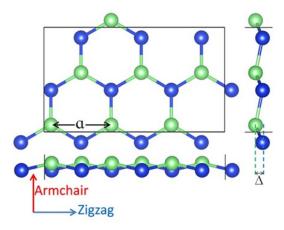


Fig. 6. Direction of armchair and zigzag on silicene nanoribbon. [14]

The intrinsic properties which make silicene effective for use in flexible electronics are the same electronic properties that have made graphene so attractive, this also includes the carrier mobility but there is an extra presence of Dirac cones which is extremely important where electronic properties are concerned as this gives the electrons movement in the x and y directions [13]. These represent given momenta within the electronic band structure of the crystal.

The intersection plays a very important role as it permits electrons to transit more easily as long as there is a small amount of energy applied to the high band. As a great percentage of electrons are located in the lower band, they are not free-flowing electrons in graphene (won't move). If a small current was applied, however, the electrons would be able to flow freely around inside the graphene. Valley polarisation is a process that is making it much simpler to study valleytronics. Valleytronics is the study of semiconductors that exploits local valleys in the electronic band structure. Certain semiconductors have multiple "valleys" in the electronic band structure [14]. Atomic configurations can be seen in Figure 6.

Valleytronics is the technology of control over the valley degree of freedom, a local maximum/minimum on the valence/conduction band, of such multivalley semiconductors.

A comparison between graphene and silicene can be seen in Figure 7.

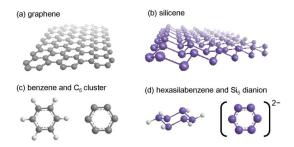


Fig. 7. Structures of Graphene and Silicene [15]

IV. MANUFACTURE OF FLEXIBLE ELECTRONICS

The main limitation of the specific candidate materials which have been explored is their production. This section of the report will review existing manufacturing methods for these candidates.

Printing techniques are used for the manufacture of flexible electronics and have been praised for their many advantages. It allows for a very efficient, largely waste-free handling of very expensive materials. It is a process that can easily be scaled up to allow for Roll-to-Roll (R2R) manufacturing at an industrial scale. There are a variety of different printing techniques, namely: screen, Inkjet, gravure, flexographic, contact and offset. Inkjet printing is the most common form - offering a way for a user to print various forms of circuitry onto substrates.

Complexities can arise with post-processing in manufacturing. The most popular metal used is silver, while it is raw material it's more expensive than copper however its stability against oxidation is advantageous. During postprocessing, copper must be operated in a form of a protective atmosphere, such as a vacuum to resist oxidation. The overall process can be seen in Figure 8.

A. Roll to Roll (R2R)

One of the main advantages of using graphene is the many ways to synthesise the material. The first approach is through mechanical exfoliation which is to isolate graphene, this method was very good at producing high quality sheets of graphene but was not very cost-effective for a productional scale.

For the use of flexible electronics, there needs to be a controlled way to mass manufacture graphene through large scale synthetic approaches. The best approach available would be the roll-to-roll production method which consists of an intermediate "buffer" layer of material which is the key to this

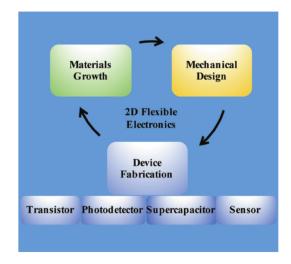


Fig. 8. Production overview of 2D materials [17]

newfound technique, this acts as a metal catalyst to perfect the roll. The production output of the film can be seen in Figure 9



Fig. 9. Roll to Roll manufacturing view [18]

The buffer material allows the graphene sheet to be lifted off from its substrate without any complications, this can allow for a more rapid roll-to-roll manufacturing process which can change the view of graphene production methodology.

B. Inkjet Printing

Inkjet printing is the primary method for the deposition of 2D 'Nano Materials' onto a substrate such as silicon wafers. This process has proven to be a fast, flexible, scalable and cost-effective method for the production of 2D flexible electronics. Inkjet printing is a form of non-contact printing, it expels the ink solution intermittently from a nozzle

onto a substrate, the application rate of droplets is controlled by a pneumatic or piezoelectric pressure exerted onto the ink reservoir [19].

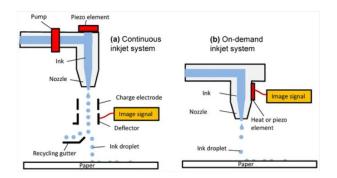


Fig. 10. Graphical representation of the inkjet printing process [20]

Due to the precision of the deposition of active materials in the range of one picolitre, it allows for minimal material waste. Prior to the ink contacting the substrate, the ink drops pass through an electric field that charges the droplets, these charged droplets are deflected by the substrate. In contrast, uncharged droplets are not deflected onto the substrate. Thus, controlling the ink flow from the reservoir onto the substrate.

To successfully project the ink onto the substrate the nanomaterials within the solution must be approximately 1/50 of the size of the nozzle diameter. In addition to this possible aggregate formation which is the clustering of nanomaterials must be avoided in the preparation of the ink otherwise it would clog the nozzle of the printer.

One of the known drawbacks to inkjet printing is its unsuitability towards low concentration ink's. However, the use of higher concentration inks boasts advantages such as reduction in printing time and improvement in the quality of the material during the evaporation of the solvents.

C. Gravure Printing

Gravure printing is a method of contact printing whereby a pattern is engraved on a metal cylinder and rolled over the substrate leaving behind the desired pattern. The viscosity of the ink used for gravure printing is between 100-1000 mPa's containing a mix of graphene and ethylcellulose or terpineol to stabilise the graphene in the solution. [21]

The ink is poured on the gravure roll, it fills the pre-made grooves in the Filling stage. Once it fills

the groves it moves to the Wiping stage where it rotates past the Doctor blade where the excess is scraped off and drops into a reservoir to be reused. The film of ink left behind after the Wiping stage is then transferred to the flexible substrate on top of the substrate carrier in the Transfer Stage. The ink print left behind after the transfer is left uneven due to the notches on the gravure roll these are left to sink to an even state in the Spreading stage of around seven nanometres with a resolution of around 100 nanometres. [22]

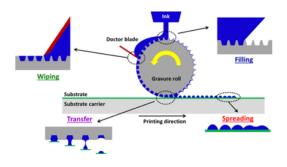


Fig. 11. Gravure Process[21]

The manufacturing process for Gravure printing has been praised for its scalability due to its utilisation of an integrated Roll-to-Roll (R2R) process to maximise throughput. This unique method of R2R boasts an impressive 1000m of material a minute.

The main type of electronics produced by this manufacturing process is Micro Supercapacitors on a flexible substrate. These flexible components hold excellent promise for the future of flexible applications due to their impressive electronic properties such as: High Specific capacitance of 6.56 mF/Cm2, Energy Density of 0.58mWh/cm2, Power Density of 14.4mW/cm3 and a 9% loss of its maximum capacitance after 1000 cycles indicating a high level of stability for use in flexible applications. [22]

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Now that the most relevant manufacturing methods have been explored, the focus of the paper can

be shifted to reviewing existing applications using the candidate materials. The purpose of this is to see the current technological capacity for us of this type of material.

V. APPLICATIONS

The output of this field can offer a plethora of new-age technologies. The aforementioned flexible displays and OLEDs are possibly the devices most recognisable by the consumer. 2D flexible electronics can prove revolutionary in many fields, such as energy harvesting and medicine.

Currently, there is extensive research being made into 2D materials which exhibit properties suitable for energy harvesting and is transparent. This could offer away in the future to apply a film to windows, allowing for another form of cheaper and greener energy source.

A. Flexible Electronics Applications using Graphene

One of the most obvious applications of flexible electronics is the use of flexible displays, for a flexible display to work you will need to have conductors that are also flexible and transparent. The main material used as the standard is indium tin oxide (ITO) as it has high performing optical properties alongside its electrical conductivity. Graphene can be used in OLED's (Organic Light Emitting Diode) as a substitute source of lighting for transparent conductor materials, this material is notably used for its tensile strength and flexibility, so it is a great replacement to ITO in theory. Although the charge carrier mobility of graphene is high it has a relatively low carrier concentration. To amend this problem, scientists have resorted to doping the material to raise the charge carrier's availability, but this needs to be done without decreasing the effectiveness of its high optical transparency. This doping is necessary as it increases efficiency in the exchange of charge carriers, this happens between the transparent electrodes and active layer.

There exists an intermediate layer in OLED's made from metal oxide film which is between the active material and the graphene electrodes. This layer creates and ensures alignment between the band and carrier flow. The active material and electrodes must be aligned even through the flexing/bending process so that modulation can happen

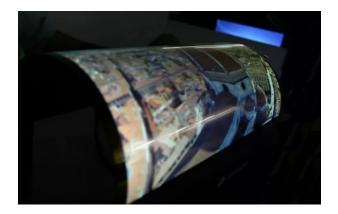


Fig. 12. Example of OLED display [23]

between the bands. This facilitates the fine-tuning of the performance specifically the optoelectronic of the device. An implemented OLED can be seen in Figure 14

The performance rates in ITO are claimed to exceed expectations due to graphene being in an early stage of development. Altho this has been claimed it's only speculation as the graphene required to exceed the set performance rates can only be manufactured by mechanical exfoliation. Mechanical exfoliation is unscalable and impractical for production. Any other production methods are unlikely to reach a higher performance as they will take even more time.

B. Flexible electronics application using silicene with a layer of hBN

Dual gated silicene Field Electronic Transistor (FET). There was a group investigation conducted for dual gate configuration with silicene based FET. Between the dielectric and the silicene layer, the FET which is made up of h-BN with silicene is inserted. The effect of this is the ability to manipulate the level of doping and change the perpendicular field. The equation for the perpendicular electric field is represented in equation 1.

$$E_1 = \frac{V_t - V_b}{d_0 - 2d_i + 2d_i/\epsilon} \tag{1}$$

The total level of doping can be reflected by the sum of the supplied voltages which have been applied to both the top and bottom gates. When the transmission spectrum was analyzed it revealed that if the perpendicular electric field has increased the device can be toggled between its ON and OFF

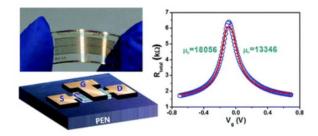


Fig. 13. Supercapacitor details [24]

state. At room temperature, the ratio of these states rests at 4.3 which is very low. This low ratio is due to the short channel length of the FET. When the length of the channel is so low the OFF-state current leakage is due to the significant tunnelling of carriers.

The hexagonal boron nitride will be used as a buffer layer, this is an important device as it's based on the pristine form of silicene. This is layer is needed due to the highly reactive nature of silicene which readily forms covalent bonds with oxygen and silicon within the atoms of the SiO2 dielectric.

The buffer layer between silicene and SiO2 stops the formation of these covalent bonds, an added advantage to this buffer layer is that both silicene and h-BN maintain their structural integrity even in the presence of other perpendicular pieces, this method is highly recommended due to this advantage.

VI. FUTURE PROSPECTS

Flexible electronics using 2D materials is a field that is still in its infancy. As seen in the limited applications that is currently used, there is a lot of room for innovation. This section will now look at the future possibilities in which this technology can be applied.

A. Medical

There are 2D materials that exhibit both properties to hold electrical circuitry and sensitivity for reading bio-data. The ability to collect data can come from skin/bone. This opens up the possibility of using molecular sensors.

The significance of molecular sensing is that it offers clinicians a way to collect data in a way previously unimaginable. A film can be applied to the skin or tooth of an individual in an unintrusive manner, and the sensors will collect data with higher

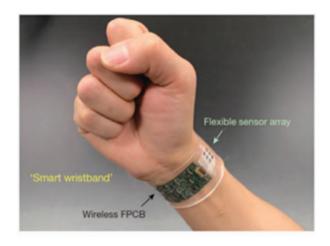


Fig. 14. Example of 2D flexible electronics used for sensing [23]

sensitivity than previously. This can lead to a fundamental change in how many aspects of the fields of medicine are conducted. A concept bracelet can be seen in 14

An important characteristic to note for sensing is the surface area to gram ratio - of which 2D flexible materials go unrivaled. [1]

B. Energy/Battries

One sector that has shown a great deal of interest is the batteries industry, specifically the challenges that can be overcome for Lithium-ion batteries. As batteries are the major key factor in the progression of portable electronics, they are coastally trying to improve efficiency by using more conductive materials and the reliability by more durable material. Not only does 2D materials provide this with higher conductive properties and increased material life is also has added benefits such as mechanical properties and many more "Moreover, these materials have shown outstanding mechanical properties, such as high Young's modulus and flexibility in comparison to their bulk counterparts".[7] It's believed that the fabrication of these batteries with 2D materials will greatly improve the lifespan and a more uniform current distribution with lower ion transfer. Due to the large surface area that 2D materials provide with the combination of tunable properties (electrical and mechanical), there seem to be endless possibilities with batteries even expanding into smart batteries where the material is sensitive enough to detect current and voltage changes accurately or if the battery is degrading and relay them back the users providing a safe and efficient system.[6]

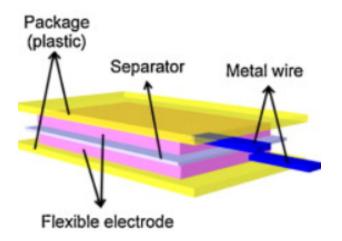


Fig. 15. Example of a 2D flexible super cap. [27]

This opens up the possibility of adding films to windows of all kinds of buildings, leading to a cheap and green form of energy harvesting. This could potentially play a part in the fight against climate change and carbon emissions.

VII. CONCLUSION

Flexible electronics using 2D materials is a field still in its infancy. Careful analysis of its manufacturing processes still shows great problems for consistency. Without the ability to consistently produce materials of similar properties, it is impossible to offer a sustainable business model in operating such a plant. Different applications demand very high-quality products with low tolerances, specifically healthcare – which is not yet possible.

The required features of flexibility, robustness and carrier mobility are vital in this field. The future of the field depends on how these characteristics can reliably be produced.

There has been a particular emphasis on carrier mobility to allow for the semiconducting aspect – with three main candidates explored: graphene, hBN and xenes. With options such as inkjet printing offering ways for manufacturing that are cost-effective, unfortunately, they do not offer any meaningful industrial scalability. Whereas, roll-to-roll and gravure printing offer the desired scalability, without the cost-effectiveness and consistency.

With the fact that the research and development into this field are still very much ongoing, processes are improving. The benefits of the outcome, i.e. the future prospects are motivation enough to create a sustainable answer.

With the possibility of the future prospect of having a monumental impact on society as it stands, it is Ultimately, the biggest constraint that exists is the scalability and cost-effectiveness of manufacture.

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