

Peer Review File

Manuscript Title: Ultra-high mobility semiconducting epitaxial graphene on silicon carbide

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referees' comments:

Referee #1 (Remarks to the Author):

This work examines the properties of a semiconducting graphene platform that emerges in the buffer layer of the well-known epitaxial graphene/SiC system when the SiC surface is prepared to a suitable level of atomic flatness.

The principal novelty is the high mobility achieved in this so-called SEG platform, in contrast to previous works where the promising semiconducting nature of the buffer layer is rendered unusable by disorder, scattering etc. induced by the rough SiC surface.

The authors further argue that semiconducting / metallic systems can be connected through hydrogen intercalation, which creates free-standing metallic regions.

Although many of the results presented here are extremely promising, the article as a whole, and in particular the discussion of the results presented, is poor.

The basic characterization presented in Fig 2 is very difficult to interpret due to nearly illegible figures, and a somewhat convoluted discussion in the text. In addition, some references to previous works get important details incorrect: e.g. Ref 21 uses DFTB and not DFT calculations to determine the band gap in the buffer layer due to periodicity effects.

Figure 3 is apparently an investigation of magnetotransport, but there is no reference to a magnetic field or its effect, instead the temperature dependence of transport is discussed, and again, rather confusingly. It is not clear what interpretation the reader is supposed to gather from the bottom panels.

A standalone discussion of epigraphene edge states is presented after the methods, and it is not clearly connected to the rest of manuscript.

The authors have an extremely promising system and set of results, but the current version of the manuscript does not do justice to these and is not suitable for publication.

Referee #2 (Remarks to the Author):

Overall scope:

This manuscript main finding concerns a novel way to grow an ordered and large -scale buffer epitaxial graphene layer with semiconducting properties. The scope is to use such layer as a semiconductor for logic components on a SiC substrate. This work may open exciting technological possibilities. However, the paper is generally poorly written, confusing and lacking key experimental demonstrations. See my detailed points below.

Overall assessment:

I see overall several key issues with the current report that need to be thoroughly addressed before potential publication:

- 1) Its novelty is based on the demonstration of the achievement of ordered, large -scale semiconducting EG. The fact that the buffer graphene may have semiconducting properties is not a novelty of this manuscript, as the authors confirm. Hence, it is critical for publication in Nature that the
 - a) emphasis on the large -scale order and reproducibility is made and clearly demonstrated throughout the manuscript. At the moment, it is not. Most measurements are very local – at the nm- μ m scales – and proof of large -scale coverage and reproducibility is absent.
 - b) More emphasis is dedicated to the details and fundamental understanding of why this sandwiched growth process would deliver order at large -scale. Also, how can the authors make sure to obtain exclusively the buffer layer over a large scale, avoiding additional graphene layers. I have not seen a Supplementary Information file in the .zip folder. I think one would like to see many more measurements, micrographs and analysis in order to be reassured of the claimed results.
 - c) The dependence of the SEG and the whole technology on the steps of SiC is not discussed well enough. I assume there are restrictions and limitations in the patterning and the placing of the devices onto the SiC. This part needs to be thoroughly discussed.
 - d) There is no proof of confidence for the reproducibility of this process, and in fact there is a rather unconvincing description about the difference between SEG 1 and SEG 2, which seem to have rather different properties, addressed with a generic “as usual samples are sporadically charged due to processing” (pg.6).
- 2) Finally, throughout the manuscript there is an unwarranted emphasis on how this technology would replace silicon -based electronics in the future. This is a bold but unfounded claim, and if this technology is demonstrated, it would find its own application without having to compete with silicon. Hence, this emphasis is really unwarranted and also unnecessary in my view, and should be toned down throughout the manuscript, starting from the title “post-silicon”.

Specific points:

- Title: the “post-silicon electronics” is misleading.
- Throughout the manuscript: epigraphene = epitaxial graphene, does not exclusively apply to epitaxial graphene from hexagonal SiC, although the latter is certainly the most prominent example
- Pg.2, second paragraph: “well -attached” does not seem a scientifically appropriate term. There are appropriate papers using suitable nomenclature and reporting factual figures that should be cited here, even though they may not refer exactly to SEG.

- Pg.3, end of the second paragraph: “DFT calculations verified that and that apart from the bandgap, the electronic properties of SEG are similar to those of graphene”. This point links back to my point 1 b) above. If SEG has bonds to the underlying SiC, this would surely affect transport properties. More elaboration is needed here to understand the breakthrough nature of this SEG.
- Source-enhanced CCS growth method: again, a lot more explanation is necessary here, either in the main paper or as supplementary information. A lot of information that is considered perhaps obvious by the authors needs to be given here (details about sandwiched approach, carbonized polymer (??), etc..)
- Fig.2 caption – there is a numbering problem, e) and f) are repeated and others are missing. Also, I don’t understand the attempt at quantifying the ID/IG ratio for SEG, as all I see is noise?
- Fig.3 – the labels of the X and Y axes are barely readable, particularly the orders of magnitude. I believe there is also an issue with the legend of the SEG series, as I cannot recognize the SEG 1 from the SEG 2 in the graphs. In addition, the difference in transport properties between the 2 samples needs to be addressed in much more detail than “due to processing”, since this manuscript aims at a new implementable technology.
- Pg 7 – the first and second paragraph contains several statements regarding SEG 1 and 2 that appear obscure, as not enough information is given on their preparation. Then the second paragraph goes on to affirm similarities of “doped SEG and QFSG”, ending with some tangential statements about networks and phase-coherent transport. Such statements need to be supported in a much more thorough way.
- Top of pg.8 – it is mentioned that the use of a better suited gate dielectric like h-BN would greatly improve mobilities. It is likely, but why has this not been implemented? I would not typically ask this for lower -impact publications, but since we are discussing publication in Nature of a new potential technology, I think this demonstration would make a lot of sense. In addition, it would be key to demonstrate that the edge state transport can be maintained even after sandwiching the graphene with a cap layer, as in the practice, for any ICs, the graphene will be buried in a stack of thin films.
- Pg 8, last paragraph “relatively inexpensive commercial single crystal....”. I would recommend removing the “relatively inexpensive” remark. It is very subjective and only few people would agree. The only thing that is sure, is that as SiC finds more large -scale applications, both pricing and availability will improve. Again, no need to compare to silicon.
- Pg 11, last paragraph. I do not understand the value and scope of this paragraph. Seems like a misplaced comment, as opposed to being part of a manuscript. Lots of generic statements with no references.
- References: there are some references that in my opinion should be replaced with more acceptable literature, with reassurance of peer-review, such as #3, #22, #46.

Referee #3 (Remarks to the Author):

In this manuscript, epigraphene with a sufficient band gap and high mobility is reported. Although graphene has high mobility, the lack of a band gap has been a major challenge in applying graphene for digital electronic devices for nearly two decades. Although many methods to introduce a band gap have been reported, the cost has always been a reduction in mobility. In such a situation, this study is a very important achievement because it provides a method to solve these problems. The

difference between this work and previous publications by the authors is that the authors essentially prepared large-area homogeneous samples and conducted electrical measurements, which is great progress. It should be noted that the results reported here also represent the culmination of 15 years of work by groups around the world in this field, including step bunching control, hydrogen intercalation, and polymer assisted sublimation growth, which indicate the significance of the present achievement by the authors. On the other hand, as a specific numerical result, 4500 cm²/Vs is not "ultrahigh" mobility for graphene. In addition, as shown below, I feel that the report is somewhat conveniently interpreted and overemphasized. Therefore, I think that the paper should be published in a journal related to Materials Science with a significant change in the representation.

1. In the Title. 4500 cm²/Vs is not "ultrahigh" mobility for graphene. Mobility value of 4525 cm²/Vs at 3.7x10¹² cm⁻² at room temperature is high for epigraphene, but not ultrahigh for graphene. This is because 35000 cm²/Vs has been reported for graphene on h-BN at 3.7x10¹² at RT (Science 342, 614 (2013)). Indeed, as the authors point out, it has an order of magnitude higher mobility than other 2D semiconductors. In addition to the higher mobility than conventional epigraphene, SEG has a band gap of 0.6 eV, which epigraphene does not have. Therefore, it should be positioned as a different material from ordinary epigraphene and many other 2D semiconductors. At least, as long as the authors include the word graphene, 4525 cm²/Vs cannot be called ultrahigh mobility.

2. In the Abstract. Millimeter scale step-free terraces seems to be an overstatement. The SE-CCS method developed by the authors caused significant step bunching, resulting in a 300 micrometer wide terrace on which a uniform buffer layer was grown. Although the the authors state "millimeter scale", the experimental evidence is not directly shown in the data, only 1 mm wide is mentioned in the text on p4. Direct evidence should be shown, because these results are quite important and challenging in this field. What is noted in the present manuscript is 300 or 500 micrometer, which should then be called sub-mm.

3. In Page 3, section of Source-enhanced CCS. The role of polymer in SE-CCS is unclear. Is the polymer also a carbon source for the buffer layer? If so, some paper on the polymer assisted sublimation growth (PASG, e.g. 2D Mater. 3, 041002 (2016)) should be cited.

4. Results shown in Figure 3. The temperature dependence of mobility shows a peculiar behavior, but the discussion is poor. In converting to the mean free path from the mobility, did you assume that the mass is constant? What is the origin of the change in the mean free path by an order of magnitude with increasing temperature? It is not considered to be phonon. Then, it is not a behavior based on the general electronic structure of graphene and needs to be discussed in detail. Also, I was very concerned about the reproducibility of experimental results such as SEG1. It shows peculiar behavior, including the presence of an inflection point around 250 K. Because this study reports an important result, reproducibility is crucial for the development of science and technology.

5. There are a total of four places in the Abstract, L5 on P6, L4 in the second paragraph of P7, and (4) in the final paragraph of P8, where it is stated that the seamless QFSG and SEG interconnects result in a quantum coherent network. What is shown experimentally in the present manuscript is that hydrogen intercalation can convert a buffer layer into QFSG, which has been known since 2009 (Phys. Rev. Lett. 103, 246804 (2009)). Also, spatially seamless interconnect has not been realized in

this study. In other words, because it has not been experimentally confirmed, it is too much emphasis. It is understandable if it is only mentioned once as a future perspective in the conclusion.

6. I do not agree with the argument that the band structures of QFSG and SEG are essentially identical except for the band gap. First, in general, materials with and without band gaps cannot be called having the identical band structure. In addition, it is not mentioned in [21] that the band structure of SEG has a Dirac-nature or linear dispersion. In other words, SEG should be understood as a two-dimensional material with a band structure different from graphene and with both high mobility and band gap.

7. The last part of the Methods section, "edge state transport," is not clearly related to the subject matter of the present manuscript. I think that it should be treated as a different work from this study.

Dear Tobias

In response to the referees, and your suggestions, we have performed many more experiments and now have measured the semiconducting properties in 9 measurement series in our cryostat. Since we had to make magnetic field sweeps at each point, these were time consuming measurements, but they were worthwhile. Not only are the measurements consistent, but they allowed us to formulate a coherent picture the transport that turns out to be rather simple, involving standard processes, like low mobility hopping transport in the impurity state and high mobility transport in the valence band (we're dealing with p doping), quantifying the transition in terms of the density of localized states, a simple mechanism for the doping (primarily due to oxygen), discerning the effects related to residual photoresist, and more. The upshot is that the localized impurity states are primarily due to photoresist and a very low density of these states (about $3 \times 10^{11}/\text{cm}^2$) occurs in samples made without resist and that UV/O₂ treatment causes high charge densities but low mobilities. The most important finding is that the mobility is reproducibly very large, especially for holes, i.e., up to $7000 \text{ cm}^2/\text{Vs}$ which is very high even for a 3D semiconductor and spectacular for a 2D semiconductor.

Furthermore, as you suggested, we spent a lot of time characterizing the production, and we concluded that a quasi-equilibrium is established between the two crystal faces at high temperature. But the production of SEG does depend on parameters like the sample polytype and the miscut of the wafer: when chips of the same wafer are used then the results are quite predictable. We tried to reduce the vast amount of data on the production so that the basic trends are clear. But it remains a bit of an art.

We also made a composite SEM image of an entire chip, of which 80% was covered with SEG and with no trace of graphene and with many large useful step free areas. An example of a 98% SEG covered sample is in Sup Mat. In fact, graphene is not found anywhere on any chip we have produced, except close to the chip edges.

We have carefully and fully responded to all the referees' requests, although a few objections and requests were not reasonable, as indicated, and we hope that you can mediate.

In any case, we stand by our original claim that this is an extremely important discovery that can change the course of 2D semiconductor research and most likely will eventually develop into a new technology, and most probably will involve more high-tech production methods than we have available in our simple little physicist's playground right now.

Yours truly,
Walt and Lei

Author Rebuttals to Initial Comment

Referee #1 (Remarks to the Author):

This work examines the properties of a semiconducting graphene platform that emerges in the buffer layer of the well-known epitaxial graphene/SiC system when the SiC surface is prepared to a suitable level of atomic flatness. The principal novelty is the high mobility achieved in this so-called SEG platform, in contrast to previous works where the promising semiconducting nature of the buffer layer is rendered unusable by disorder, scattering etc. induced by the rough SiC surface. The authors further argue that semiconducting / metallic systems can be connected through hydrogen intercalation, which creates free-standing metallic regions. Although many of the results presented here are extremely promising, the article as a whole, and in particular the discussion of the results presented, is poor.

Authors Reply: Thank you so much for your encouraging remarks. The paper has been rewritten entirely, involving much new data. We hope that the discussion is much complete, and the paper is much better now.

The basic characterization presented in Fig 2 is very difficult to interpret due to nearly illegible figures, and a somewhat convoluted discussion in the text. In addition, some references to previous works get important details incorrect: e.g. Ref 21 uses DFTB and not DFT calculations to determine the band gap in the buffer layer due to periodicity effects.

Authors Reply: Figure 2 has been vastly improved, and the discussion has been made more logical. We have contacted the author of Ref. 21. It is fact that a DFT calculation where it counts, for example that is to get the correct molecular interactions. In fact, as for all DFT calculations, the bandgap is underestimated. The referees' objections are well taken.

Figure 3 is apparently an investigation of magnetotransport, but there is no reference to a magnetic field or its effect, instead the temperature dependence of transport is discussed, and again, rather confusingly. It is not clear what interpretation the reader is supposed to gather from the bottom panels.

Authors Reply: That is correct. We wished to distinguish Hall mobilities from FET mobilities. We have now removed that label. These panels mean to emphasize the difference between QFSG and SEG, since the former is derived from the latter. In any case, those panels were removed from the main text and placed in Methods section in the context of future developments of the technology. A standalone discussion of epigraphene edge states is presented after the methods, and it is not clearly connected to the rest of manuscript. Moreover, the references to the edge state have been removed.

The authors have an extremely promising system and set of results, but the current version of the manuscript does not do justice to these and is not suitable for publication.

Authors Reply: We have greatly increased the volume of data. Rather than one series of measurements, we now have 9 that provide a coherent picture of the doping process and the transition from hopping conductance through localized states to band conduction. We show that room temperature Hall mobilities $> 1000 \text{ cm}^2/\text{Vs}$ are readily achieved and that the localized state densities can be as small as $3 \times 10^{11}/\text{cm}^2$. We hope that the referee is satisfied with the current presentation.

Referee #2 (Remarks to the Author):

Overall scope:

This manuscript main finding concerns a novel way to grow an ordered and large -scale buffer epitaxial graphene layer with semiconducting properties. The scope is to use such layer as a semiconductor for logic components on a SiC substrate. This work may open exciting technological possibilities. However, the

paper is generally poorly written, confusing and lacking key experimental demonstrations. See my detailed points below.

Authors Reply: We thank the referee for his frank and thorough assessment of the paper and we hope that this thoroughly modified version with more complete experimental results will satisfy his/her reservations.

Overall assessment:

I see overall several key issues with the current report that need to be thoroughly addressed before potential publication:

1) Its novelty is based on the demonstration of the achievement of ordered, large -scale semiconducting EG. The fact that the buffer graphene may have semiconducting properties is not a novelty of this manuscript, as the authors confirm. Hence, it is critical for publication in Nature that the a) emphasis on the large -scale order and reproducibility is made and clearly demonstrated throughout the manuscript. At the moment, it is not. Most measurements are very local – at the nm- μ m scales – and proof of large -scale coverage and reproducibility is absent.

Authors Reply: Thank you for your suggestion and comment. In the current version we have vastly increased the volume of data. We now present a composite SEM image of a complete 3.5mm x 4.5 mm wafer with more than 80 % coverage of SEG, within which there are many areas on the order of 200 μ m x 300 μ m that are completely step free. Moreover, often we observe step free terraces that are over 1 mm long and over 100 μ m wide. We now provide ample examples in the main text and in Sup Mat.

b) More emphasis is dedicated to the details and fundamental understanding of why this sandwiched growth process would deliver order at large -scale. Also, how can the authors make sure to obtain exclusively the buffer layer over a large scale, avoiding additional graphene layers. I have not seen a Supplementary Information file in the .zip folder. I think one would like to see many more measurements, micrographs and analysis in order to be reassured of the claimed results.

Authors Reply: Thank you for your suggestion. In the present version, we have developed the hypothesis of a quasi-equilibrium between the top and bottom chip, with experimental evidence. We also added a large number of micrographs and other evidence in the Sup Mat. We literally have not seen any of graphene on any of the samples we have made except very close to the edges where the two chips do not overlap. We do see large patches of bare SiC, usually in the middle of the chips. However, our current recipes are reliable enough so that a chip will be at least covered by 50% of its surface with SEG, however the size of the step free domains is not fully under control but there are enough areas of at least 100 μ m x 100 μ m for research sized devices on the chips that we produce routinely.

c) The dependence of the SEG and the whole technology on the steps of SiC is not discussed well enough. I assume there are restrictions and limitations in the patterning and the placing of the devices onto the SiC. This part needs to be thoroughly discussed.

Authors Reply: As mentioned in the answer of the previous question, we do have to select useful areas to avoid steps. But this process is straightforward, since the SEG covered areas can quickly be identified either with an SEM or the optical microscope or the Raman spectrometer, which allows for Raman verification as well. We certainly agree that our present method is not yet ready for industrial applications, although it will be if we succeeded in perfection on better controlling of the corralling method in future as envisioned in the text. There are no real patterning limitations, besides identifying suitable patterning areas, which are abundant. We believe that the current presentation, and in particular Fig. 2e makes this point clear.

d) There is no proof of confidence for the reproducibility of this process, and in fact there is a rather unconvincing description about the difference between SEG 1 and SEG 2, which seem to have rather different properties, addressed with a generic “as usual samples are sporadically charged due to processing” (pg.6).

Authors Reply: This point has been thoroughly addressed. We now have increased a number of SEG samples that were used for in depth transport studies from 1 to 6, on which have performed 9 measurement series. Note that each data point in Fig. 9 takes about 1-2 hours, because the temperature in the cryostat must be stabilized after which a magnetic field sweep (typically from -3T to +3T) was performed. The charging by oxygen in our case is now fully explained and analyzed in detail. The different transport regimes are identified, and coherently explained. Doping by oxygen and the effect of residual photoresist residues is comprehensively addressed. A method to determine the localized state densities (i.e. the densities of states in the band gap) is demonstrated and we explicitly show that devices that have not been subjected to photoresist have significantly fewer localized states. We also demonstrate that charge density increase, and the mobility decrease by UV irradiation in the presence of O₂. We believe that we have fully and comprehensively provided the experimental evidence that the referee has requested.

2) Finally, throughout the manuscript there is an unwarranted emphasis on how this technology would replace silicon -based electronics in the future. This is a bold but unfounded claim, and if this technology is demonstrated, it would find its own application without having to compete with silicon. Hence, this emphasis is really unwarranted and also unnecessary in my view, and should be toned down throughout the manuscript, starting from the title “post-silicon”.

Authors Reply: We have toned down the language as the referee requested, although we would like to point out that there are over 50 papers in Nature and 75 papers in Science on graphene that discuss their results with reference to post-silicon electronics. Also, while it is a long shot for sure, this is in fact our goal as it has been since 2001 when we started our work on epitaxial graphene electronics. I guess physicist tend to have unreasonable lofty goals to keep them going.

Specific points:

- Title: the “post-silicon electronics” is misleading.

Authors Reply: The phrase has been removed.

- Throughout the manuscript: epigraphene = epitaxial graphene, does not exclusively apply to epitaxial graphene from hexagonal SiC, although the latter is certainly the most prominent example

Authors Reply: This is not entirely accurate. In fact, years ago I have coined the phrase epigraphene which specifically represents the graphene that is epitaxially grown on SiC: before we called it epitaxial graphene, which was problematic for the reasons that exactly the referee pointed out. But we really cannot help that others now have coopted our definition of epigraphene and misapply it to any form of epitaxial graphene on any substrate. We prefer not to again invent a new name to sort out this confusion.

- Pg.2, second paragraph: “well -attached” does not seem a scientifically appropriate term. There are appropriate papers using suitable nomenclature and reporting factual figures that should be cited here, even though they may not refer exactly to SEG.

Authors Reply: We have removed the phase, which was used in the context of exfoliated graphene. More specifically, the adhesion of exfoliated graphene to SiO₂ surfaces, which can be heavily contaminated and often incorrectly attributed to the van der Waals interaction.

- Pg.3, end of the second paragraph: “DFT calculations verified that and that apart from the bandgap, the electronic properties of SEG are similar to those of graphene”. This point links back to my point 1 b) above. If SEG has bonds to the underlying SiC, this would surely affect transport properties. More elaboration is needed here to understand the breakthrough nature of this SEG.

Authors Reply: Thank you for your comments. We have checked with Alberto Sorbelli who is author of the TBDF calculations in question, and he explained that he did not provide simplistic picture that was presented in the paper (Nair et al.). He gave an elaborate answer. In fact the bonding to the substrate is somewhere between covalent and van der Waals depending of the relative orientation of the Si atoms and the C atoms (i.e. the pyramidalization angle). Ultimately about ¼ of the surface Si atoms are covalently bonded. We believe that the resulting band structure is correct, and in fact in the relevant paper, the authors compare it with graphene, showing that the density of states, besides at band gap are really remarkably similar (see Fig. 5 e in Nano. Lett. 2017 doi: 10.1021/acs.nanolett.7b00509). But the reason that we now avoid elaborating on this point is that except the existence of the band gap and a reasonable approximation of the density of states, we really don't need more to explain the basic transport properties, as we have done in the Fig. 3 now. We further note that phonon scattering is weak, as it is in graphene, and the scattering is primarily from ionized impurities, again as is also seen in graphene.

- Source-enhanced CCS growth method: again, a lot more explanation is necessary here, either in the main paper or as supplementary information. A lot of information that is considered perhaps obvious by the authors needs to be given here (details about sandwiched approach, carbonized polymer (??), etc..)

Authors Reply: In order to understand the SEG formation method a lot of work have been conducted, relevant information is included both in the modified manuscript and SI. Accordingly, a new furnace has been built (i.e. the vertical furnace, see Fig. 5) in which the temperature gradient can be better controlled. We also have supplied more information along the lines that the referee requested in Sup Mat. More importantly that we found that the polymer is not required in the new system and a quasi-equilibrium between the two chips is proposed and justified.

- Fig.2 caption – there is a numbering problem, e) and f) are repeated and others are missing. Also, I don't understand the attempt at quantifying the ID/IG ratio for SEG, as all I see is noise?

Authors Reply: Thank you for your comments and suggestions. All the figures and captions are now revised. As far as the 2D/1G ratio is concerned, the point is that SEG has no 2D peak, which is in fact a measure of the amount of graphene. In graphene, this ratio is about 2, the results evidence that there is no graphene on the surface. We hope that the present version makes this clearer.

- Fig.3 – the labels of the X and Y axes are barely readable, particularly the orders of magnitude. I believe there is also an issue with the legend of the SEG series, as I cannot recognize the SEG 1 from the SEG 2 in the graphs. In addition, the difference in transport properties between the 2 samples needs to be addressed in much more detail than “due to processing”, since this manuscript aims at a new implementable technology.

Authors Reply: As mentioned above, we have performed many more transport measurements that are now coherently explained (please see the above discussion).

- Pg 7 – the first and second paragraph contains several statements regarding SEG 1 and 2 that appear

obscure, as not enough information is given on their preparation. Then the second paragraph goes on to affirm similarities of “doped SEG and QFSG”, ending with some tangential statements about networks and phase-coherent transport. Such statements need to be supported in a much more thorough way.

Authors Reply: All obscure and tangential statements have now been removed or clarified.

- Top of pg.8 – it is mentioned that the use of a better suited gate dielectric like h-BN would greatly improve mobilities. It is likely, but why has this not been implemented? I would not typically ask this for lower - impact publications, but since we are discussing publication in Nature of a new potential technology, I think this demonstration would make a lot of sense. In addition, it would be key to demonstrate that the edge state transport can be maintained even after sandwiching the graphene with a cap layer, as in the practice, for any ICs, the graphene will be buried in a stack of thin films.

Authors Reply: The main point of this paper is to demonstrate the semiconducting properties of SEG, not to demonstrate an immediately implementable technology. This probably was not clear in the original manuscript, and we hope that it is clearly addressed in the present version. In fact, we have an entire research program and several publications dedicated to producing h-BN on epigraphene. Much progress has been made, and we hope to someday have a Nature article dedicated to that alone, which would relieve many researchers from having obtain h-BN flakes from one or two suppliers worldwide, exfoliating, transfer and patterning it etc. but with no guarantee of success.

- Pg 8, last paragraph “relatively inexpensive commercial single crystal...”. I would recommend removing the “relatively inexpensive” remark. It is very subjective and only few people would agree. The only thing that is sure, is that as SiC finds more large -scale applications, both pricing and availability will improve. Again, no need to compare to silicon.

Authors Reply: In fact, the issue of the price of SiC has come up often in the literature in assessing the value of epigraphene research. is a quote in ‘A roadmap for graphene’, Nature 490, 192–200 (2012) commenting on Epigraphene:

“The two major drawbacks of this method are the high cost of the SiC wafers and the high temperatures (above 1,000 °C) used,”

In fact, today the cost of 1 cm² electronics grade SiC (Cree) is \$12, which probably is much less than general reader thought, so personally, I think that the record should be set straight.

The exact expression “Graphene has emerged as one of the most promising materials for the post-silicon era” is endlessly repeated, even in Nature articles and now.

We hope that the editor can suggest some relevant statement in this paper that can address this rather important point in an acceptable way.

- Pg 11, last paragraph. I do not understand the value and scope of this paragraph. Seems like a misplaced comment, as opposed to being part of a manuscript. Lots of generic statements with no references.

Authors Reply: It has been rewritten in a more appropriate way.

- References: there are some references that in my opinion should be replaced with more acceptable literature, with reassurance of peer-review, such as #3, #22, #46.

Authors Reply: Reference 3 has been removed and replaced with a peer reviewed journal paper. As for the others, they refer to theses that have not yet resulted in papers. We believe that PhD theses are

legitimate references, but of course caution is warranted. Here we do not use them to prove any cardinal point in the paper.

Referee #3 (Remarks to the Author):

In this manuscript, epigraphene with a sufficient band gap and high mobility is reported. Although graphene has high mobility, the lack of a band gap has been a major challenge in applying graphene for digital electronic devices for nearly two decades. Although many methods to introduce a band gap have been reported, the cost has always been a reduction in mobility. In such a situation, this study is a very important achievement because it provides a method to solve these problems. The difference between this work and previous publications by the authors is that the authors essentially prepared large-area homogeneous samples and conducted electrical measurements, which is great progress. It should be noted that the results reported here also represent the culmination of 15 years of work by groups around the world in this field, including step bunching control, hydrogen intercalation, and polymer assisted sublimation growth, which indicate the significance of the present achievement by the authors. On the other hand, as a specific numerical result, $4500 \text{ cm}^2/\text{Vs}$ is not "ultrahigh" mobility for graphene. In addition, as shown below, I feel that the report is somewhat conveniently interpreted and overemphasized. Therefore, I think that the paper should be published in a journal related to Materials Science with a significant change in the representation.

Authors Reply: We thank the referee for carefully examining the paper and his/her detailed comments. However, the referee apparently does not be convinced that this paper is suitable for Nature even its main point was correct, i.e. that we have discovered a semiconducting form of graphene which has mobility of $4500 \text{ cm}^2/\text{Vs}$. We disagree with that conclusion, since several recent Nature articles 2D semiconductors with mobilities even 2 orders of magnitude smaller and less stable than the one what we demonstrate here, which already suggests a breakthrough in this sense. Incidentally, our more recent experiments with better samples, these values have increased to $7000 \text{ cm}^2/\text{Vs}$, and we will not be surprised if it ends up being even larger than that. Moreover, I also believe it is somewhat misleading to compare SEG with graphene. I completely agree that a room temperature graphene mobility under $100,000 \text{ cm}^2/\text{Vs}$ will not raise any eyebrows. But this is a 2D semiconductor with a hole mobility that is an order of magnitude larger than hole mobilities in silicon, therefore it is a different story.

1. In the Title. $4500 \text{ cm}^2/\text{Vs}$ is not "ultrahigh" mobility for graphene. Mobility value of $4525 \text{ cm}^2/\text{Vs}$ at $3.7 \times 10^{12} \text{ cm}^{-2}$ at room temperature is high for epigraphene, but not ultrahigh for graphene. This is because $35000 \text{ cm}^2/\text{Vs}$ has been reported for graphene on h-BN at 3.7×10^{12} at RT (Science 342, 614 (2013)). Indeed, as the authors point out, it has an order of magnitude higher mobility than other 2D semiconductors. In addition to the higher mobility than conventional epigraphene, SEG has a band gap of 0.6 eV, which epigraphene does not have. Therefore, it should be positioned as a different material from ordinary epigraphene and many other 2D semiconductors. At least, as long as the authors include the word graphene, $4525 \text{ cm}^2/\text{Vs}$ cannot be called ultrahigh mobility.

Authors Reply: Here again, I am not sure it is proper to compare graphene mobilities with semiconducting graphene mobilities. Also, the suggestion that semiconducting graphene should be positioned as a different material than ordinary epigraphene is not coherent with the fact that the buffer layer has been described as semiconducting graphene in the past decades in high impact papers. For us this nomenclature is justified, we believe that the editor may want to weigh in on an eventual name change, which I am sure will be confusing to many in the field.

2. In the Abstract. Millimeter scale step-free terraces seems to be an overstatement. The SE-CCS method developed by the authors caused significant step bunching, resulting in a 300 micrometer wide terrace on

which a uniform buffer layer was grown. Although the the authors state "millimeter scale", the experimental evidence is not directly shown in the data, only 1 mm wide is mentioned in the text on p4. Direct evidence should be shown, because these results are quite important and challenging in this field. What is noted in the present manuscript is 300 or 500 micrometer, which should then be called sub-mm.

Authors Reply: While, the referee is correct that we do not see domains that are over 1 mm in both dimensions, we often seen domains that are much more than 1 mm long but they are usually not wider than 300 μm . We have adjusted the relevant expressions accordingly.

3. In Page 3, section of Source-enhanced CCS. The role of polymer in SE-CCS is unclear. Is the polymer also a carbon source for the buffer layer? If so, some paper on the polymer assisted sublimation growth (PASG, e.g. 2D Mater. 3, 041002 (2016)) should be cited.

Authors Reply: In fact, the polymer is not between the two chips but on the outside the sandwich on the Si-face of the bottom chip. Its role is not fully understood yet, and in the present paper we show that the polymer need not be used (see Fig. 5 in Methods). As before we believe that the actual role of the polymer is to enhance the temperature difference between the two chips, which is an important growth parameter (among several others as explained in the current version).

4. Results shown in Figure 3. The temperature dependence of mobility shows a peculiar behavior, but the discussion is poor. In converting to the mean free path from the mobility, did you assume that the mass is constant? What is the origin of the change in the mean free path by an order of magnitude with increasing temperature? It is not considered to be phonon. Then, it is not a behavior based on the general electronic structure of graphene and needs to be discussed in detail. Also, I was very concerned about the reproducibility of experimental results such as SEG1. It shows peculiar behavior, including the presence of an inflection point around 250 K. Because this study reports an important result, reproducibility is crucial for the development of science and technology.

Authors Reply:

- (1) We agree with the referee that it is not correct to assume a constant mass. In the new version we do not mention mean free paths, only mobilities, which are well defined.
- (2) In the present version, the change in the mobility is explained in terms of a transition from hopping transport in the localized states in the energy gap to band transport, which is usually the reason for the change in mobility in semiconductor when the Fermi level cross the conduction (or valence) band edge. A detailed discussion has been included into the revised version.
- (3) As in graphene, we have no evidence for significant phonon scattering in the temperature range of the experiment. We explain all of the transport properties quite conventionally in terms of the transition from hopping transport to band transport and scattering from charged impurities.
- (4) We have not reproduced the unusual kink at 250 K (which is now Sample S-22 in Fig. 4) in any of the other 8 measurement series that we have performed.
- (5) We agree that reproducibility and coherent explanations are crucial. We believe that the current version satisfies these criteria.

5. There are a total of four places in the Abstract, L5 on P6, L4 in the second paragraph of P7, and (4) in the final paragraph of P8, where it is stated that the seamless QFSG and SEG interconnects result in a quantum coherent network. What is shown experimentally in the present manuscript is that hydrogen intercalation can convert a buffer layer into QFSG, which has been known since 2009 (Phys. Rev. Lett. 103, 246804 (2009)). Also, spatially seamless interconnect has not been realized in this study. In other

words, because it has not been experimentally confirmed, it is too much emphasis. It is understandable if it is only mentioned once as a future perspective in the conclusion.

Authors Reply: We have removed statements about QFSG from the main article and only kept them in the methods section in the context of future advances. We also show a QFSG/SEG/QFSG junction, but its transport measurements have not been demonstrated; We have demonstrated a functioning graphene/buffer/graphene junction pair in prior work, as cited in the paper.

6. I do not agree with the argument that the band structures of QFSG and SEG are essentially identical except for the band gap. First, in general, materials with and without band gaps cannot be called having the identical band structure. In addition, it is not mentioned in [21] that the band structure of SEG has a Dirac-nature or linear dispersion. In other words, SEG should be understood as a two-dimensional material with a band structure different from graphene and with both high mobility and band gap.

Authors Reply: This conclusion was not drawn by us, it was made in an article on the buffer layer (Nano. Lett. 2017 Vol. 17 Issue 4 Pages 2681-2689). We trust the correctness of DFTB calculated band structure. There, the comparison shows the remarkable similarity of the density of states of the two (see Fig. 5 e). We contacted the theorist who made the density functional calculation to confirm this correspondences. In any case, we believe that our characterization is correct.

7. The last part of the Methods section, "edge state transport," is not clearly related to the subject matter of the present manuscript. I think that it should be treated as a different work from this study.

Authors Reply: Thank you for your comment and suggestion. The edge state work has been removed accordingly.

Reviewer Reports on the First Revision:

Referees' comments:

Referee #1 (Remarks to the Author):

The authors have significantly revised and rewritten the manuscript since the first round of review, and much of the discussion has been significantly improved.

Many of the confusing issues that I raised in my first report have been satisfactorily addressed. They have also performed additional experiments to highlight the robustness of the fabrication process.

There remain some issues with the presentation, particularly with Figs 2&3 and the associated discussion in the main text. Firstly, most of the subpanel references to Fig 2 (a, b, c, d, etc.) in the text are inconsistent with the Figure itself.

The superposition of Raman spectra on top of the map in panel c is next to illegible.

Secondly, the discussion in terms of arbitrarily numbered samples is difficult to follow across the various panels in Fig 3. It would be significantly easier to follow if the samples were clearly grouped beforehand, as the distinctions between them, or why certain features only occur for certain samples, is not clear.

Nonetheless, the authors clearly have a result of high impact on their hands here: a robust, scalable platform for semiconducting graphene electronics. This is significant enough to warrant publication in Nature, once the presentation issues are fully addressed.

Referee #2:

recommends publication

Referee #3 (Remarks to the Author):

I have carefully reviewed the considerably revised manuscript, and the authors' reply. Regarding reproducibility of the experiment, which was the biggest concern, the results of sufficient additional experiments have been reported. On the other hand, analysis and discussion of the additional experiments are very poor again. And I felt as a whole that the manuscript was hard to read because some of the results were just added like in Fig.3. And some were just placed in Figs. 5-10 and they are not described in the main text almost at all. At present, it is not suitable for publication in Nature. I strongly recommend to reconstruct the whole manuscript (main text and figures), because I believe that the content is quite good.

Some specific comments:

1. Page 2

Epigraphene, buffer layer and semiconducting graphene (SEG) are introduced, referring the Sup. Mat. However, essential difference between the buffer layer and SEG is not still clear. I felt that they are essentially the same, but high-quality buffer layer without disorder could be successfully grown in this study. Then, I am not convinced to use "semiconducting graphene".

In addition to this point, I recommend to use only "buffer layer". This use will also be helpful to avoid confusion about the discussion I raised in my previous comment "use of ultra-high mobility graphene is not appropriate because it is not graphene". I also suggest the title to be for example "Ultra-high mobility 2D semiconducting buffer layer on silicon carbide".

2. Page 4

In the paragraph of Surface characterization, "we find that in a wide range of temperatures graphene is absent to any detectible level". What do you mean by "in a wide range of temperatures"? Are they growth temperatures? Is it about the results shown in Supplementary materials? If so, which ones? Please clearly indicate the corresponding figures.

And, the arrangement of figures introduction is not sophisticated, appearing in the scattering position.

3. Page 5

I agree that "oxygen is readily adsorbed by the buffer layer". But in order to say that the change of the carrier density is due to oxygen, more experimental evidence is required. In other words, "oxygen electron affinity on the buffer layer is 0.12 eV" is too speculative.

4. Page 5 and the corresponding figures and their caption

The unit used in this study is S and Ohm, then, conductance and resistance should be used instead of conductivity and resistivity.

5. Page 5

"This increase in the mobility is seen in 2D and 3D semiconductors, and it is attributed to a transition from low mobility hopping transport between localized state at low temperatures to band transport in delocalized at high temperatures". This is too speculative. At least, the authors should clearly show that the temperature dependence of the conductance can be fitted using hopping transport at low temperatures and using band transport at high temperatures. It is an easy task.

6. Figure 1c

Add z-scale in the AFM images.

7. Figure 3c

The mobilities at room temperature seem to be about 200, 350, 1000, 2000, 3000, 3000, 5000, and 5500. There is no plot showing 7000 cm^2/Vs .

8. Methods

Use of semi-insulating SiC should be clearly written. We have experienced the similar temperature dependence like Fig. 3 in the measurements of graphene on n-doped SiC (0001).

In the second paragraph, Figures are not referred appropriately. "Fig. 1a, middle" should be Fig. 1c, middle. Same are Fig. 1a, Fig. 2d, Fig. 2e.

Is LFM lateral force microscopy? Or, is it LAFM as defined in Page4? Is it Fig. 5b?
Fig. 2b seems to be LEED, but it appears as Raman spectroscopy. ...and so on.
...Too many mistakes and inconsistency!!

9. Figures 5-10

Meaning and positioning of figures 5-10 is not clearly written in the main text. They should be omitted, described clearly in the text, or transferred into SI. I suggest to reconstruct the whole manuscript.

Author Rebuttals to First Revision:

Responses to referees

Referee #1 (Remarks to the Author):

The authors have significantly revised and rewritten the manuscript since the first round of review, and much of the discussion has been significantly improved. Many of the confusing issues that I raised in my first report have been satisfactorily addressed. They have also performed additional experiments to highlight the robustness of the fabrication process.

We thank the referee for his/her kind comments and the time spent going over the manuscript carefully.

There remain some issues with the presentation, particularly with Figs 2&3 and the associated discussion in the main text. Firstly, most of the subpanel references to Fig 2 (a, b, c, d, etc.) in the text are inconsistent with the Figure itself.

We have fixed the problems with Figs.2 and 3 that the referee is refereeing to.

The superposition of Raman spectra on top of the map in panel c is next to illegible. Secondly, the discussion in terms of arbitrarily numbered samples is difficult to follow across the various panels in Fig 3. It would be significantly easier to follow if the samples were clearly grouped beforehand, as the distinctions between them, or why certain features only occur for certain samples, is not clear.

We have redrawn Figure 3 and made it more legible. We have relabeled the samples to make the discussion of them easier to follow.

Nonetheless, the authors clearly have a result of high impact on their hands here: a robust, scalable platform for semiconducting graphene electronics. This is significant enough to warrant publication in Nature, once the presentation issues are fully addressed.

We thank the referee for his/her positive final judgement of the paper.

Referee #3 (Remarks to the Author):

I have carefully reviewed the considerably revised manuscript, and the authors' reply. Regarding

reproducibility of the experiment, which was the biggest concern, the results of sufficient additional experiments have been reported.

We thank the referee for carefully reading the paper and being satisfied with the modifications and apologize for the annoying defects that made the refereeing process more tedious than needed.

As a whole that the manuscript was hard to read because some of the results were just added like in Fig.3. And some were just placed in Figs. 5-10 and they are not described in the main text almost at all. At present, it is not suitable for publication in Nature. I strongly recommend to reconstruct the whole manuscript (main text and figures), because I believe that the content is quite good.

We agree with all the referee's objections, and we have followed his/her recommendations. The paper was reconstructed and simplified. The Methods section was rewritten, and the figures are now discussed in more detail in the main text (i.e., in the Methods section).

1. Page 2

Epigraphene, buffer layer and semiconducting graphene (SEG) are introduced, referring the Sup. Mat. However, essential difference between the buffer layer and SEG is not still clear. I felt that they are essentially the same, but high-quality buffer layer without disorder could be successfully grown in this study. Then, I am not convinced to use "semiconducting graphene".

In addition to this point, I recommend to use only "buffer layer". This use will also be helpful to avoid confusion about the discussion I raised in my previous comment "use of ultra-high mobility graphene is not appropriate because it is not graphene". I also suggest the title to be for example "Ultra-high mobility 2D semiconducting buffer layer on silicon carbide".

We understand the referees' objections to the use of the term SEG. However, we would like to point out that the buffer layer has had several different names in the past. It was originally called the $6\sqrt{3}$ structure or $6\sqrt{3}$ reconstruction. (van Bommel 1997). Next it was called the Nano-mesh (Forbeau PhysRevB.58.16396 1996 and others), then it was called the 0-layer and finally the buffer layer (multiple authors). Buffer layer is non-descript and used certainly not unique to the $6\sqrt{3}$ reconstruction of the 0001 face of h-SiC as a quick google search shows. Buffer layer is generic for the $6\sqrt{3}$ reconstruction regardless of the degree of disorder which varies significantly in conventionally (vacuum) produced buffer layer. Moreover, It is usual to give the ordered crystalline manifestation of a material a different name than the disordered form (glass/quartz, glassy carbon/ diamond, aluminum oxide/sapphire, etc.). So, if this material turns out to be important in the future, it will only be cumbersome and-confusing if it is referred to as the "well-ordered buffer layer on silicon carbide". SEG (semiconducting epigraphene) is concise, accurate and unambiguous.

Also, the previous title *did not* contain the phrase *ultra-high mobility graphene* but rather “ultra-high *mobility semiconducting* graphene” which is obviously essentially different. We request that the title remains unchanged.

2. Page 4

In the paragraph of Surface characterization, "we find that in a wide range of temperatures graphene is absent to any detectable level". What do you mean by "in a wide range of temperatures"? Are they growth temperatures? Is it about the results shown in Supplementary materials? If so, which ones? Please clearly indicate the corresponding figures. And, the arrangement of figures introduction is not sophisticated, appearing in the scattering position.

We have modified this statement as follows:

“ Using a combination of these measurements we find that do not find evidence for graphene either on the plateaus or on the substrate steps in samples produced in the face-to-face method as described here. As shown in Fig. 2a, the surfaces are either coated with SEG or they are bare SiC.”

The subpanel figures in Fig. 2 have been aligned in the conventional way.

3. Page 5

I agree that "oxygen is readily adsorbed by the buffer layer". But in order to say that the change of the carrier density is due to oxygen, more experimental evidence is required. In other words, "oxygen electron affinity on the buffer layer is 0.12 eV" is too speculative.

We agree with the referee that we should avoid characterizing the experimentally determined ΔE in the Arrhenius analysis as the electron affinity and we have removed that qualification. However, we are quite confident that the charging is due to oxygen as was previously found by Turmaud (Sup Mat). Moreover, we show in the modified version of the paper (Fig. 3c) that the extrapolations of the linear fits to the Arrhenius plots converge to about $1500 \times 10^{12} / \text{cm}^2$ at $T=\infty$ ($1/T=0$) which is close to the expected density of a monolayer of O_2 on the surface as would be expected if indeed a physisorbed O_2 molecule absorbs one electron from the SEG. Nevertheless, we now do not claim that the doping is from adsorbed O_2 but suggest that it is *consistent with* the observations.

4. Page 5 and the corresponding figures and their caption

The unit used in this study is S and Ohm, then, conductance and resistance should be used instead of conductivity and resistivity.

On page 5 we have included the sentence:

"Note that in 2D materials resistivities are expressed in Ohms and conductivities in Siemens.", since this is the usual convention in 2D materials and already used in the earliest graphene papers. We know that some authors use Ohms/square for 2D resistivities and Siemens/square for conductivities of 2D materials, but it is as far as we know, not conventional.

5. Page 5

"This increase in the mobility is seen in 2D and 3D semiconductors, and it is attributed to a transition from low mobility hopping transport between localized state at low temperatures to band transport in delocalized at high temperatures". This is too speculative. At least, the authors should clearly show that the temperature dependence of the conductance can be fitted using hopping transport at low temperatures and using band transport at high temperatures. It is an easy task.

We agree with the referee that a more thorough analysis of the transition from hopping conductivity to band conductivity would be desirable, but it is not an easy task since we cannot probe the low temperature behavior and we do not have a gated structure. In fact, any form of disorder in a semiconductor produces states in the gap where transport is due to one or more of several hopping mechanisms and sorting that out is not trivial. However, a transition from low mobility transport involving localized states to high mobility band transport is always observed. For example, Turmaud (see Sup Mat) has explicitly demonstrated that for the buffer layer that transport closely follows Mott's variable range hopping model (rather than the alternative Efros-Shklovskii variable range hopping model) and since the major difference between buffer layer and SEG is the defect density it is reasonable that we assume that we also are observing the similar processes without specifying the precise localized state transport model that is operative.

In the revised version we delve deeper into this issue (see Fig. 3d and the discussion on page 5) where we identify the charge density at which the localized transport to band conduction occurs and correlate it the defect densities which in turn is related to the sample production method.

We believe that the current discussion is adequate and both qualitatively and quantitatively consistent with observations in previous work of our group (Turmaud) on the buffer layer and by other groups on other 2D materials.

6. Figure 1c

Add z-scale in the AFM images.

We thank referee's suggestion, and the relevant scale has been added to the modified figure.

7. Figure 3c

The mobilities at room temperature seem to be about 200, 350, 1000, 2000, 3000, 3000, 5000, and 5500. There is no plot showing 7000 cm²/Vs.

The referee is correct. We do not show data with a mobility of 7000 cm²/Vs. We have modified the manuscript and figure caption accordingly.

8. Methods

Use of semi-insulating SiC should be clearly written. We have experienced the similar temperature dependence like Fig. 3 in the measurements of graphene on n-doped SiC (0001). In the second paragraph, Figures are not referred appropriately. "Fig. 1a, middle" should be Fig. 1c, middle. Same are Fig. 1a, Fig. 2d, Fig. 2e. Is LFM lateral force microscopy? Or, is it LAFM as defined in Page4? Is it Fig. 5b? Fig. 2b seems to be LEED, but it appears as Raman spectroscopy. ...and so on. ...Too many mistakes and inconsistency!!

We thank the referee for his/her comments, and we apologize for the annoying errors. The Methods section was not well written and has been rewritten. We now clearly indicate that we use semi-insulating SiC (page 2, SEG production).

It LFM is indeed lateral force microscopy, and we made the appropriate specification.

Other typo's have been fixed.

9. Figures 5-10

Meaning and positioning of figures 5-10 is not clearly written in the main text. They should be omitted, described clearly in the text, or transferred into SI. I suggest to reconstruct the whole manuscript.

We have reconstructed the whole manuscript and the Methods section has been made more coherent. We hope that the information conveyed in the Methods section is now more informative. We do understand that there are several topics discussed here but we followed the recommendations of the editor the best we could on this point.