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To Whom It May Concern:

I am pleased to serve as external member of the thesis committee for Carlo Bernard, Department of Physics, University of Zürich, and to herewith submit my evaluation of his thesis carried out under the supervision of Professor Thomas Greber.

I am presently a Professor of Electrical and Computer Engineering at the University of Nebraska-Lincoln (USA). I hold a Ph.D. degree in Physics from ETH Zürich (Switzerland) and have about 20 years of postdoctoral academic experience. My primary research interests and expertise are in the fields of two-dimensional (2D) materials, surface science, and in-situ microscopy using scanning probe, cathode-lens and transmission electron microscopes. Some of these areas strongly overlap with the topics or Mr. Bernard's dissertation. I am familiar with the journal articles on which the dissertation is based, and I have also been involved in several meetings, presentations, and discussions of the reported results.

The present dissertation is based primarily on Mr. Bernard's contributions to six peer-reviewed journal articles published between 2014 and 2018:

1. *"High quality single atomic layer deposition of hexagonal boron nitride on single crystalline Rh(111) four-inch wafers"*, Review of Scientific Instruments 85, 035101 (2014).
2. *"Fermi surface map of large-scale single-orientation graphene on SiO_2"*, Journal of Physics: Condensed Matter 29, 475001 (2017).
3. *"Flattening and manipulation of the electronic structure of h-BN/Rh(111) nanomesh upon Sn intercalation"*, Surface Science 672-673, 33 (2018).
4. *"Remote doping of graphene on SiO_2 with 5 keV x-rays in air"*, Journal of Vacuum Science & Technology A 36, 020603 (2018).
5. *"Centimeter-sized single-orientation monolayer hexagonal boron nitride with or without nanovoids"*, Nano Letters 18, 1205 (2018).
6. *"Electronic properties of transferable atomically thin $MoSe_2$/h-BN heterostructures grown on Rh(111)"*, ACS Nano 10.1021/acsnano.8b05628.

Although he was not the lead author on any of these papers, it is clear from the thesis and from my involvement on his dissertation committee that Mr. Bernard made significant contributions to all of them. At the same time, the thesis reports several as yet unpublished results that appear of high interest and would warrant wider dissemination, time permitting. Overall, I conclude that *Mr. Bernard's contributions are clearly at a high level and are, in quality as well as scope, sufficient and appropriate for a Ph.D. dissertation.*

The dissertation itself is structured logically. It begins with a general introduction, followed by a thorough discussion of the background knowledge, primarily the fairly broad range of experimental techniques relevant to the presented research: Sample preparation by chemical vapor deposition, characterization using photoelectron spectroscopy, photoelectron diffraction, angle-resolved photoelectron spectroscopy, low-energy electron diffraction, scanning tunneling microscopy, Raman spectroscopy, and electronic transport (resistivity & Hall effect). The thesis also briefly summarizes the salient features of the electronic structures of the main materials of interest: Single-layer graphene and

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hexagonal boron nitride. *These sections of the dissertation are generally well written and scientifically correct, and demonstrate an in-depth understanding of the broader concepts underlying the dissertation research.* I would like to note here in particular the *breadth of experimental methods*, with which Mr. Bernard familiarized himself in the course of his thesis research.

The narrative of the dissertation shows *good knowledge and use of the literature in the field.* The *references are generally correct and appropriate*. In a few cases, additional citations would be in order. Corresponding suggestions, along with input on editorial aspects and typing errors, have been sent directly to the candidate and his supervising professor.

The primary research topics reflected in the thesis can be divided roughly into three categories: (i) Growth of graphene and hexagonal boron nitride on metal surfaces, and delamination/transfer of the single-layer honeycomb materials, individually or as van der Waals stacks, to insulating substrates; (ii) characterization of the pristine materials using a broad range of surface science methods; and (iii) characterization of the transferred monolayers and heterostructures using electronic transport measurements, Raman spectroscopy, etc. Over the past decade, there has been intense research activity – both experimental and theoretical – focused on 2D materials and heterostructures. Distinct from most of this work, the goal of Mr. Bernard's research has been the demonstration of methods for *wafer-scale synthesis and transfer* of high-quality graphene and h-BN. Addressing these issues is timely and of high interest since it could help enable future applications of these materials, for example in post-silicon nanoelectronics. While the overall goal of developing scalable synthesis and transfer methods remains, to some extent, a work in progress, I conclude that *Mr. Bernard has made significant contributions toward this long-term goal* and that *his results and their discussion in the thesis should be deemed sufficient to earn him a doctoral degree*.

Several specific results are particularly noteworthy. For example, Mr. Bernard succeeded in growing high-quality graphene and h-BN on Sinergia wafers, the scalable silicon based platform with epitaxial metal top layers at the heart of his thesis research; and he transferred these films to SiO_2 and measured their electrical transport properties both as individual layers and as stacked heterostructures. *Experimentally realizing all of the involved process steps has clearly presented considerable challenges*. While perhaps not altogether satisfactory, the results have demonstrated the feasibility of the underlying concept. As a critical remark, I would note that the work has perhaps not taken optimal advantage of one of the key characteristics of 2D crystals: The ease with which their carrier concentration can be tuned by electrostatic gating. The lack of systematic gated transport measurements limits the impact of the results, since the reported resistivities and carrier mobilities hold only for the native doping state of the materials, which is almost certainly different for the different samples. Nevertheless, I applaud Mr. Bernard for taking on the difficult task of transferring on-metal synthesized 2D materials to a platform where technologically important properties can be measured and, in the future, optimized.

A second important example of Mr. Bernard's contributions is the attempt to directly grow vertical van der Waals heterostructures, here of graphene on h-BN, by chemical vapor deposition. *This idea has been circulating for some time in the literature, but has turned out to be extremely challenging to realize*. Mr. Bernard's work systematically explores this concept via UHV CVD of h-BN on Sinergia Rh(111), followed by exposure to carbon-rich precursors at near-ambient pressure. The results, obtained mainly by a rich suite of surface science methods, are interesting. The main conclusion, namely that the sequential growth process leads to lateral instead of vertical heterostructures, may be disappointing but in view of previous reports perhaps not unexpected. In my critique of the work, I would note that a few questions could perhaps be addressed more squarely. For instance, while it is concluded that carbon during the second growth step displaces h-BN, the atomistic mechanism remains unclear and is also not evident (or clearly discussed in the thesis) why the carbon atoms should arrange in graphene patches, which are then nicely laterally bonded to the remaining h-BN. Also the question of a possible Rh-carbide remains open and would be interesting to address conclusively.

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Finally, I note the collaborative work with Prof. Andras Kis' group on heterostructures involving transition metal dichalcogenides, in particular $MoSe_2$. Here, *Mr. Bernard's work opened up new territory toward the broad application of scalable, wafer-sized graphene and h-BN films*. Besides fabricating high-quality h-BN films, on which the collaborators grew $MoSe_2$ by molecular beam epitaxy, Mr. Bernard also carried out commendable work in characterizing the resulting heterostructures using photoelectron spectroscopy, photoelectron diffraction, and low-energy electron diffraction. Notably absent is further characterization by imaging. Scanning tunneling microscopy, for example, could have helped shed light on some of the questions regarding thickness variations, domain sizes, crystal quality, rotational order, etc. Overall, however, *I again conclude that Mr. Bernard's contribution are on a high level and certainly meet the standards required for original research toward a doctoral degree*.

As a critical remark, I note that the final chapters, namely the Conclusions and Outlook are perhaps not as polished as the other chapters of the thesis. Here, some additional work could enhance the overall impression of the thesis. My suggestion is to distill away the details of the previous thesis chapters and to focus on the most important results, their impact on the broader field, and their implications for future work by the group and by researchers at large.

In conclusion, I state that the dissertation overall is well-written, scientifically sound and logical in structure. The suggested corrections sent to the candidate are largely editorial in nature. In a few instances *citing additional references should be considered, and additional discussion of the results would be in order. I regard the required corrections as minor*, and have already communicated my suggestions directly to the candidate and his supervising professor. I do not need to see the corrected version before permission to publish the dissertation is granted. I am pleased to congratulate Mr. Bernard. He has achieved a commendable body of work of international stature and has written a fine dissertation. *I recommend that permission to publish the dissertation be granted.*

Sincerely,

P. Sutter

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