

STRAIN ENGINEERING OF THE ELECTRONIC STRUCTURE OF 2D MATERIALS

del CORRO Elena¹, PEÑA-ÁLVAREZ Miriam^{1,2}, MORALES-GARCÍA Ángel³, BOUŠA Milan^{1,3},
ŘÁHOVÁ Jaroslava^{1,3}, KAVAN Ladislav¹, KALBÁČ Martin¹, FRANK Otakar^{1,*}

¹*J. Heyrovsky Institute of Physical Chemistry of the AS CR, v.v.i., Prague, Czech Republic, EU,*
* otakar.frank@jh-inst.cas.cz

²*Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid,*
Spain, EU

³*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague,*
Czech Republic, EU

Abstract

The research on graphene has attracted much attention since its first successful preparation in 2004. It possesses many unique properties, such as an extreme stiffness and strength, high electron mobility, ballistic transport even at room temperature, superior thermal conductivity and many others. The affection for graphene was followed swiftly by a keen interest in other two dimensional materials like transition metal dichalcogenides. As has been predicted and in part proven experimentally, the electronic properties of these materials can be modified by various means. The most common ones include covalent or non-covalent chemistry, electrochemical, gate or atomic doping, or quantum confinement. None of these methods has proven universal enough in terms of the devices' characteristics or scalability. However, another approach is known - mechanical strain/stress, but experiments in that direction are scarce, in spite of their high promises.

The primary challenge consists in the understanding of the mechanical properties of 2D materials and in the ability to quantify the lattice deformation. Several techniques can be then used to apply strain to the specimens and thus to induce changes in their electronic structure. We will review their basic concepts and some of the examples so far documented experimentally and/or theoretically.

Keywords: 2D materials, graphene, electronic structure, strain engineering, mechanical properties

1. INTRODUCTION

With the isolation of a single layer of graphene [1], a whole new world of two-dimensional (2D) materials opened up [2]. They all possess specific, often unique properties, dramatically different from the properties of their bulk progenitors. Among others, graphene is the strongest [3] and thermally most conductive [4] material known, with exceptional electrical conductivity and transport characteristics even at room conditions [5]. Graphene is a zero band-gap semiconductor. The other 2D materials span the whole range of electronic characteristics, from the isolating hexagonal boron nitride, via semiconducting to metallic transition metal dichalcogenides [6]. In many of these materials, their electronic structure changes with the decreasing number of layers, e.g. bulk MoS₂ is an indirect band-gap semiconductor, while its monolayer counterpart has a direct band-gap [7]. And similarly to graphene/graphite, most of the single layer materials have better mechanical properties compared to the bulk.

Considering all the above mentioned characteristics of 2D materials, it is straightforward to imagine their future applications in various fields, especially in optoelectronics. However, there is one particular feature of the 2D materials, which makes their prospective high-tech utilization even more appealing - but complicating in the same time - the ease of manipulating their electronic structure by external perturbations. In the following text, we will briefly review first the prerequisite for the strain engineering, namely the mechanical properties of 2D materials and how the imposed strain can be monitored, then the basic concepts of manipulating the electronic structure in graphene and transition metal dichalcogenides (TMDC), especially in MoS₂ (as the most scrutinized 2D material apart from graphene).

2. MECHANICAL PROPERTIES

In spite of its extreme stiffness, strength and strain to failure, it is very difficult to conduct standard mechanical tests of graphene due to its monoatomic thickness and the associated arduous handling [8]. Therefore, most of the so far recovered values of various mechanical properties have been obtained through indentation tests of graphene suspended over holes (**Fig. 1**) and successive modelling. The first such experiment on exfoliated graphene yielded Young's modulus of 1 TPa, intrinsic strength of 130 GPa, axial breaking strength of 42 Nm^{-1} , and in-plane stiffness of 340 Nm^{-1} [3]. The typical fracture forces for these samples suspended over circular holes with diameters of 1-1.5 μm were $\sim 1.7 \text{ }\mu\text{N}$ [3]. The same kind of experiment carried out on graphene grown by chemical vapor deposition (CVD) showed the dominant role of grain boundaries in these samples (**Fig. 1e-f**), which resulted in the decrease of the fracture loads to $\sim 100 \text{ nN}$, hence more than an order of a magnitude lower than for single-crystalline exfoliated samples [9]. Finally, the indentation experiment was repeated on exfoliated graphene, but this time bombarded by Ar ions inducing a random distribution of vacancy-type defects (**Fig. 1a-d**) [10]. As expected, the fracture force dropped quickly to $\sim 0.6 \text{ }\mu\text{N}$ as the defects appeared. However, counterintuitively, the value of Young's modulus increased up to the defect content of $\sim 0.2 \%$, and started to decrease only after reaching this threshold. The initial increase in Young's modulus was explained in terms of a dependence of the elastic coefficients on the momentum of flexural modes predicted for two-dimensional membranes [10].

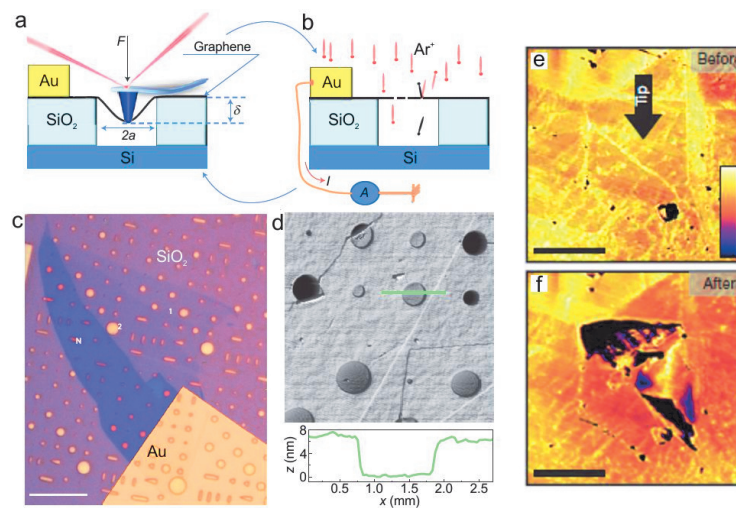


Fig. 1 Experimental setup of indented graphene suspended over holes [10]: (a) Device geometry and scheme of the nanoindentation set-up, which uses an AFM tip for mechanical testing, (b) Irradiation set-up, where the defects are induced by the incoming argon ions (red), (c) optical microscopy image of exfoliated graphene contacted by a gold electrode deposited on an array of wells (scale bar: 15 μm), (d) AFM image (top view) of a graphene sheet covering several circular wells (green line length: 2.7 μm). (e-f) AFM phase images of a CVD graphene grain before and after an indentation measurement [9]: (e) indentation takes place at the center of this grain as shown by the arrow, (f) the region is torn along grain boundaries after indentation (scale bars: 200 nm). Reprinted by permission from Macmillan Publishers Ltd: Nature Physics [10] and Nature [9], © 2015 and 2011, resp.

Raman spectroscopy is the mostly used method for monitoring the lattice deformation in graphene and other 2D materials [11]. In general, Raman spectroscopy assesses the phonons, which soften upon tension and harden upon compression. Hence the shifts in frequencies of the peaks in Raman spectra reflect directly the strain level [8,12], and through a further analysis of the results, stress can be obtained too [13]. Most of the experiments conducted so far on graphene include biaxial tension (e.g., in pressurized bubbles on holed substrates), hydrostatic compression, or uniaxial tension or compression on graphene supported by polymeric beams [8]. Apart from the strain level, these experiments can provide Grüneisen parameters of the measured phonons. In the case of uniaxial strain, the lattice orientation of the studied samples can be easily obtained

through the G band splitting [8,14]. Additionally, out-of-plane deformation (buckling) during uniaxial compression can be assessed and quantified [15]. On the other hand, the analysis of the spectra is often complicated due to charge transfer (e.g., from the substrate), which affects the Raman spectra too [16]. In some specific cases, the effects of strain and doping can be disentangled via a careful analysis of several parameters of the Raman peaks [17], however, a care has to be taken to analyze larger sets of data for that purpose and preferably to avoid drawing conclusions based on the acquisition of a single spectrum.

3. STRAIN ENGINEERING IN GRAPHENE

Mechanical stress is known to offer different ways of manipulating the electronic structure of graphene [8,18]. Band-gap opening is surely the mostly discussed trait in this direction, however, it has been a subject of many disputes in the literature [19]. In spite of early optimistic reports on the possible band-gap opening [20], later tight-binding and density functional theory calculations showed that in monolayer (1L) graphene it is almost impossible to induce a permanent band-gap by the sole application of uniaxial strain [19,21]. The crucial point of the calculation lies in the proper sampling of the strained Brillouin zone, which shows indeed a “gap” at the K points, but no real band-gap at the Dirac points (**Fig. 2a**) - the K points and the Dirac points do not coincide. When the sampling is scarce, this fact can be (and was) missed. In spite of the infeasibility of band-gap opening by pure axial strain, the theory predicts that a combination with either shear strain [21] or periodic corrugations [22] can decrease the needed strain level to more reasonable values, however, still above 10%. Even lower strain levels should be sufficient to induce band-gap opening in bilayer graphene, again with a simultaneous application of inhomogeneous or out-of-plane stress [23]. It should be noted that no such band-gap opening has been unequivocally evidenced in an experiment yet. A possible indication of a band-gap opening has been reported in uniaxially strained bilayer graphene with inhomogeneities (**Fig. 2c**) induced by sandwiching the sample between polymer layers [24].

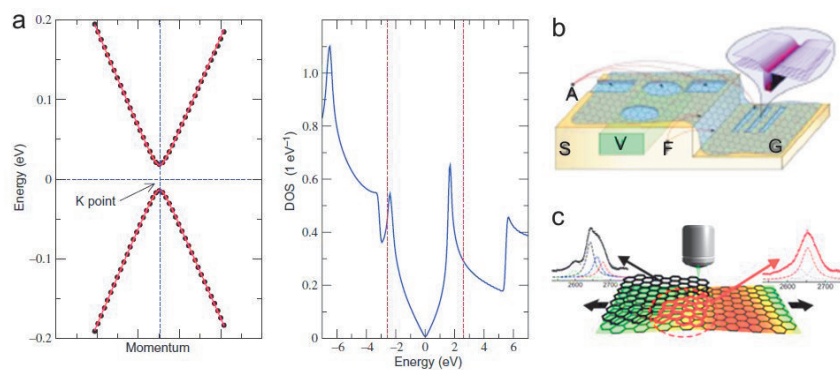


Fig. 2 (a) Fictitious band-gap at K point in 1L graphene at 1% uniaxial strain while no band appears in the DOS [19]. © IOP Publishing & Deutsche Physikalische Gesellschaft. CC BY-NC-SA. (b) A sketch of possible strain engineering of graphene by substrate patterning [25]: substrate (S) patterned with folds (F), trenches, dots and wells (A), upon which rests a graphene sheet (G). Reprinted with permission of APS, © 2009. (c) A sketch of possible band-gap opening in inhomogeneously strained bilayer graphene, monitored by Raman spectroscopy [24].

Further possible utilization of strain engineering of the electronic structure of graphene lies in the creation of localized structures, e.g. through substrate patterning, to achieve direction-dependent tunneling, beam collimation or quantum confinement (0D or 1D) [25]. Strain is also predicted to induce pseudomagnetic gauge fields exceeding 10 T [26]. Experimentally, this effect was documented using scanning tunneling microscopy on graphene nanobubbles grown on Pt(111) surface, which showed Landau levels corresponding to pseudomagnetic fields greater than 300 T [27].

4. STRAIN ENGINEERING IN TRANSITION METAL DICHALCOGENIDES

Strain engineering in TMDCs represents a different task compared to graphene, owing to the 3D structure of their individual layers. Hence manipulating the positions of individual atoms within the cells readily influences the potentials, bond strengths and superpositions (overlaps) of atomic orbitals (e.g., 3p for S and 4d for Mo), which are directly responsible for most of the partial density of states in the material. Recently, several theoretical and/or experimental works appeared showing the influence of strain on the band structure of MoS₂, clearly demonstrating the importance of the strain orientation on the band-gap change [28-34]. Monolayer and bilayer MoS₂ samples were subjected to small uniaxial tensile strains (up to 2%) through bending of their polymeric substrates [29]. The direct optical gap of monolayer MoS₂ redshifted alongside with the decreasing of the intensity of the corresponding photoluminescence band, and the transition to an indirect band-gap appeared at ~1.3% of strain [29]. Under hydrostatic conditions, the band-gap energy in monolayer MoS₂ was shown first to increase, and then at ~ 10-19 GPa to decrease and to change to an indirect band-gap [30,32]. The transition to a metallic state is predicted to take place at pressures higher than ~ 60 GPa [32]. On the other hand, as we have shown recently [33], direct out-of-plane compression results a quick transition from direct to indirect band-gap (at ~ 0.5 GPa) and the transition to a metallic state happens at 2-3 GPa. The band gap energy decreases almost linearly with the increasing stress [33].

MoS₂ offers another interesting asset, which might find its use, e.g., in photovoltaics - exciton funneling. Wrinkles in few layer MoS₂ (**Fig. 3a**) were shown to induce such effect, namely the funneling of photogenerated excitons from flat regions of the sample to the wrinkles [28]. The wrinkles serve as traps with a local confinement potential for excitons. A model based on a gradually, non-uniformly strained monolayer MoS₂ has been predicted to generate a so-called broad-spectrum solar energy funnel (Fig. 3b), working on a similar principle [35].

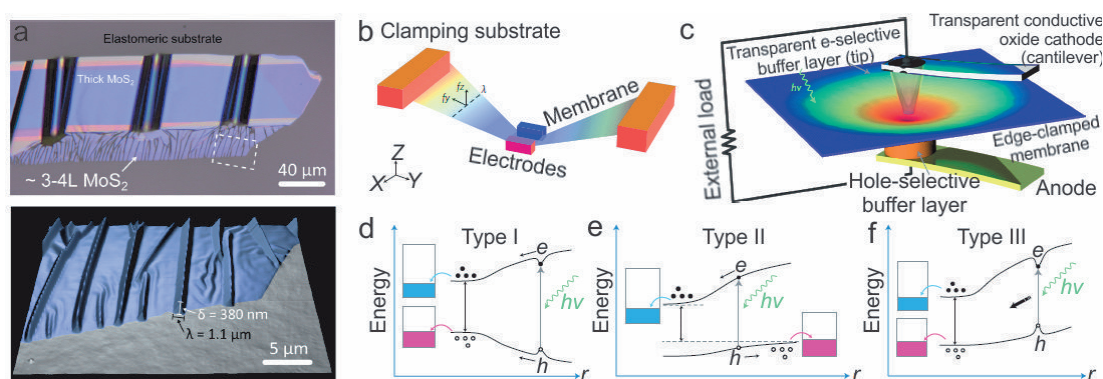


Fig. 3 (a) Wrinkles in a few-layer MoS₂ on an elastomeric substrate. Reprinted with permission from [28]. © 2013 American Chemical Society. (b-f) Schematics of introducing inhomogeneous strain and classifying funnelling mechanisms [35]: (b) Inhomogeneously strained membrane ribbon with varying width. The two electrodes mechanically impose a vertical displacement on the central region of the membrane. (c) Setup for elastic strain-engineered artificial atom (not drawn to scale). (d-f) Three solar energy funnelling mechanisms arising from a different band bending and exciton binding profile in the strain-engineered semiconducting membrane. Reprinted by permission from Macmillan Publishers Ltd: Nature Photonics [35], © 2012.

5. CONCLUSION

As we have outlined, strain engineering has an unprecedented ability to manipulate the electronic structure of 2D materials to almost any extent. On the other hand, majority of the works are still theoretical or, if experimental, not yet with the repeatability needed for a serious application. Yet the first works and concepts promise an even brighter future for low-dimensional materials.

ACKNOWLEDGEMENTS

This work is supported by Czech Science Foundation (project nr. 14-15357S).

REFERENCES

- [1] NOVOSELOV, K.S., GEIM, A.K., MOROZOV, S.V., JIANG, D., ZHANG, Y., DUBONOS, S.V., GRIGORIEVA, I.V., FIRSOV, A.A. Electric field effect in atomically thin carbon films. *Science*, 2004, vol. 306, nr. 5296, p. 666-669.
- [2] GEIM, A.K., MACDONALD, A.H. Graphene: Exploring carbon flatland. *Physics Today*, 2007, vol. 60, nr. 8, p. 35-41.
- [3] LEE, C., WEI, X.D., KYRIS, J.W., HONE, J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science*, 2008, vol. 321, nr. 5887, p. 385-388.
- [4] BALANDIN, A.A. Thermal properties of graphene and nanostructured carbon materials. *Nature Materials*, 2011, vol. 10, nr. 8, p. 569-581.
- [5] NOVOSELOV, K.S., FALCO, V.I., COLOMBO, L., GELLERT, P.R., SCHWAB, M.G., KIM, K. A roadmap for graphene. *Nature*, 2012, vol. 490, nr. 7419, p. 192-200.
- [6] NOVOSELOV, K.S., JIANG, D., SCHEDIN, F., BOOTH, T.J., KHOTKEVICH, V.V., MOROZOV, S.V., GEIM, A.K. Two-dimensional atomic crystals. *Proceedings of the National Academy of Sciences of the United States of America*, 2005, vol. 102, nr. 30, p. 10451-10453.
- [7] MAK, K., LEE, C., HONE, J., SHAN, J., HEINZ, T. Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Physical Review Letters*, 2010, vol. 105, nr. 13, p. 136805.
- [8] GALIOTIS, C., FRANK, O., KOUKARAS, E.N., SFYRIS, D. Graphene Mechanics: Current Status and Perspectives. *Annual Review of Chemical and Biomolecular Engineering*, 2015, vol. 6, p. 121-140.
- [9] HUANG, P.Y., RUIZ-VARGAS, C.S., VAN DER ZANDE, A.M., WHITNEY, W.S., LEVENDORF, M.P., KEVEK, J.W., GARG, S., ALDEN, J.S., HUSTEDT, C.J., ZHU, Y., PARK, J., MCEUEN, P.L., MULLER, D.A. Grains and grain boundaries in single-layer graphene atomic patchwork quilts. *Nature*, 2011, vol. 469, nr. 7330, p. 389-392.
- [10] LOPEZ-POLIN, G., GOMEZ-NAVARRO, C., PARENTE, V., GUINEA, F., KATSNELSON, M.I., PEREZ-MURANO, F., GOMEZ-HERRERO, J. Increasing the elastic modulus of graphene by controlled defect creation. *Nature Physics*, 2015, vol. 11, nr. 1, p. 26-31.
- [11] FERRARI, A.C., BASKO, D.M. Raman spectroscopy as a versatile tool for studying the properties of graphene. *Nature Nanotechnology*, 2013, vol. 8, nr. 4, p. 235-246.
- [12] YOUNG, R.J., KINLOCH, I.A., GONG, L., NOVOSELOV, K.S. The mechanics of graphene nanocomposites: A review. *Composites Science and Technology*, 2012, vol. 72, nr. 12, p. 1459-1476.
- [13] ANDROULIDAKIS, C., TSOUKLERI, G., KOUTROUMANIS, N., GKIKAS, G., PAPPAS, P., PARTHENIOS, J., PAPAGELIS, K., GALIOTIS, C. Experimentally derived axial stress-strain relations for two-dimensional materials such as monolayer graphene. *Carbon*, 2015, vol. 81, nr. 0, p. 322-328.
- [14] MOHIUDDIN, T.M.G., LOMBARDO, A., NAIR, R.R., BONETTI, A., SAVINI, G., JALIL, R., BONINI, N., BASKO, D.M., GALIOTIS, C., MARZARI, N., NOVOSELOV, K.S., GEIM, A.K., FERRARI, A.C. Uniaxial strain in graphene by Raman spectroscopy: G peak splitting, Grueneisen parameters, and sample orientation. *Physical Review B*, 2009, vol. 79, nr. 20, p. 205433-205438.
- [15] ANDROULIDAKIS, C., KOUKARAS, E.N., FRANK, O., TSOUKLERI, G., SFYRIS, D., PARTHENIOS, J., PUGNO, N., PAPAGELIS, K., NOVOSELOV, K.S., GALIOTIS, C. Failure Processes in Embedded Monolayer Graphene under Axial Compression. *Scientific Reports*, 2014, vol. 4, p. 5271.
- [16] FRANK, O., DRESSELHAUS, M.S., KALBAC, M. Raman Spectroscopy and in Situ Raman Spectroelectrochemistry of Isotopically Engineered Graphene Systems. *Accounts of Chemical Research*, 2015, vol. 48, nr. 1, p. 111-118.
- [17] LEE, J.E., AHN, G., SHIM, J., LEE, Y.S., RYU, S. Optical separation of mechanical strain from charge doping in graphene. *Nature Communications*, 2012, vol. 3, p. 1024.
- [18] BISSETT, M.A., TSUJI, M., AGO, H. Strain engineering the properties of graphene and other two-dimensional crystals. *Physical Chemistry Chemical Physics*, 2014, vol. 16, nr. 23, p. 11124-11138.
- [19] RIBEIRO, R.M., PEREIRA, V.M., PERES, N.M.R., BRIDDON, P.R., NETO, A.H.C. Strained graphene: tight-binding and density functional calculations. *New Journal of Physics*, 2009, vol. 11, p. 115002.

- [20] NI, Z.H., YU, T., LU, Y.H., WANG, Y.Y., FENG, Y.P., SHEN, Z.X. Uniaxial Strain on Graphene: Raman Spectroscopy Study and Band-Gap Opening. *Acs Nano*, 2008, vol. 2, nr. 11, p. 2301-2305.
- [21] COCCO, G., CADELANO, E., COLOMBO, L. Gap opening in graphene by shear strain. *Physical Review B*, 2010, vol. 81, nr. 24, p. 241412.
- [22] NAUMOV, I.I., BRATKOVSKY, A.M. Gap opening in graphene by simple periodic inhomogeneous strain. *Physical Review B*, 2011, vol. 84, nr. 24, p. 245444.
- [23] CHOI, S.-M., JHI, S.-H., SON, Y.-W. Controlling Energy Gap of Bilayer Graphene by Strain. *Nano Letters*, 2010, vol. 10, nr. 9, p. 3486-3489.
- [24] FRANK, O., BOUŠA, M., RIAZ, I., JALIL, R., NOVOSELOV, K.S., TSOUKLERI, G., PARTHENIOS, J., KAVAN, L., PAPAGELIS, K., GALIOTIS, C. Phonon and Structural Changes in Deformed Bernal Stacked Bilayer Graphene. *Nano Letters*, 2012, vol. 12, nr. 2, p. 687-693.
- [25] PEREIRA, V.M., NETO, A.H.C. Strain Engineering of Graphene's Electronic Structure. *Physical Review Letters*, 2009, vol. 103, nr. 4, p. 046801-046804.
- [26] LOW, T., GUINEA, F. Strain-Induced Pseudomagnetic Field for Novel Graphene Electronics. *Nano Letters*, 2010, vol. 10, nr. 9, p. 3551-3554.
- [27] LEVY, N., BURKE, S.A., MEAKER, K.L., PANLASIGUI, M., ZETTL, A., GUINEA, F., NETO, A.H.C., CROMMIE, M.F. Strain-Induced Pseudo-Magnetic Fields Greater Than 300 Tesla in Graphene Nanobubbles. *Science*, 2010, vol. 329, nr. 5991, p. 544-547.
- [28] CASTELLANOS-GOMEZ, A., ROLDÁN, R., CAPPELLUTI, E., BUSCEMA, M., GUINEA, F., VAN DER ZANT, H.S.J., STEELE, G.A. Local Strain Engineering in Atomically Thin MoS₂. *Nano Letters*, 2013, vol. 13, nr. 11, p. 5361-5366.
- [29] CONLEY, H.J., WANG, B., ZIEGLER, J.I., HAGLUND, R.F., PANTELIDES, S.T., BOLOTIN, K.I. Bandgap Engineering of Strained Monolayer and Bilayer MoS₂. *Nano Letters*, 2013, vol. 13, nr. 8, p. 3626-3630.
- [30] DOU, X., DING, K., JIANG, D., SUN, B. Tuning and Identification of Interband Transitions in Monolayer and Bilayer Molybdenum Disulfide Using Hydrostatic Pressure. *Acs Nano*, 2014, vol. 8, nr. 7, p. 7458-7464.
- [31] HE, K., POOLE, C., MAK, K.F., SHAN, J. Experimental Demonstration of Continuous Electronic Structure Tuning via Strain in Atomically Thin MoS₂. *Nano Letters*, 2013, vol. 13, nr. 6, p. 2931-2936.
- [32] NAYAK, A.P., PANDEY, T., VOIRY, D., LIU, J., MORAN, S.T., SHARMA, A., TAN, C., CHEN, C.-H., LEE, L.-J., CHHOWALLA, M., LIN, J.-F., SINGH, A.K., AKINWANDE, D. Pressure-Dependent Optical and Vibrational Properties of Monolayer Molybdenum Disulfide. *Nano Letters*, 2015, vol. 15, nr. 1, p. 346-353.
- [33] PEÑA-ÁLVAREZ, M., DEL CORRO, E., MORALES-GARCÍA, Á., KAVAN, L., KALBAC, M., FRANK, O. Single Layer Molybdenum Disulfide under Direct Out-of-Plane Compression: Low-Stress Band-Gap Engineering. *Nano Letters*, 2015, vol. 15, nr. 5, p. 3139-3146.
- [34] SCALISE, E., HOUSSA, M., POURTOIS, G., AFANAS'EV, V., STESMANS, A. Strain-induced semiconductor to metal transition in the two-dimensional honeycomb structure of MoS₂. *Nano Research*, 2012, vol. 5, nr. 1, p. 43-48.
- [35] FENG, J., QIAN, X., HUANG, C.-W., LI, J. Strain-engineered artificial atom as a broad-spectrum solar energy funnel. *Nature Photonics*, 2012, vol. 6, nr. 12, p. 866-872.