IL NUOVO CIMENTO **47 C** (2024) 289
DOI 10.1393/ncc/i2024-24289-2

Communications: SIF Congress 2023

Single photon emission from hydrogen-filled transition metal dichalcogenide bubbles

F. Tuzi(*), S. Cianci and E. Blundo(**)
Physics Department, Sapienza University of Rome - Rome, Italy

received 1 March 2024

Summary. — Single-photon emitters (SPEs) have been observed in strained single layers of Transition Metal Dichalcogenides (TMDs) at cryogenic temperatures. Several approaches have been investigated, but the achievement of regular arrays of controllably strained areas, and thus of controlled SPEs, remains a challenge. Here, we discuss the possibility of exploiting strained single-layered TMD bubbles containing highly pressurised hydrogen, which can be controllably created in an ordered fashion by lithography-based approaches. While these structures would deflate at cryogenic temperatures due to the liquefaction of hydrogen, we discovered that the deposition of few-layer-thick hexagonal boron nitride (hBN) on top of the TMD bubbles allows them to maintain their shape, even for temperatures as low as 5 K. By performing Raman measurements on the bubbles, we were able to track the strain behaviour of the system at different temperatures, showing that biaxial strains as high as 1.6% are achieved even at 5 K. Micro-photoluminescence (μ-PL) studies of hBN-capped WS_2 bubbles at cryogenic temperatures demonstrated the presence of quantum emitters on the edges of several bubbles. The SPEs were characterised through magneto-μ-PL and time-resolved measurements.

1. – Introduction

Monolayers (MLs) of TMDs subject to strain, achieved either through a deformation (*e.g.*, wrinkles) of the layer during deposition or by laying the ML on top of pre-formed nanostructures, were shown to enable the observation of single photon emitters (SPEs) at cryogenic temperatures in multiple studies [1-4]. These studies highlighted the key role played by strain in activating/brightening the emitters. While the use of patterned substrates has enabled the achievement of arrays of SPEs, the proposed methods, however, allow for a scarce control over the strain transferred to the MLs. Furthermore, the obtained strain values are typically small. Here, we investigate the potentiality of hydrogen-filled, highly-strained 1-layer-thick TMD bubbles for the achievement of SPEs

(*) E-mail: `federico.tuzi@uniroma1.it`
(**) E-mail: `elena.blundo@uniroma1.it`

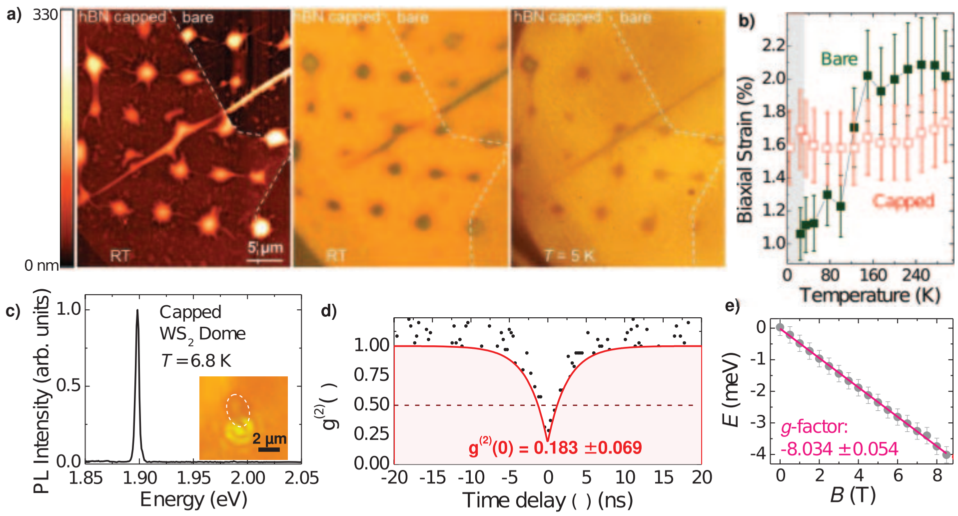

Fig. 1. – (a) Left: AFM image of an ordered array of WS_2 bubbles. The left side of the array is capped with few-layer-thick hBN, as delineated by the white dashed line, while the bubbles on the top-right are left bare. Centre-Right: Optical microscope image of the same array, taken at RT (centre) and at $T = 5$ K (right). Remarkably, at 5 K, the bubbles capped by hBN remained in shape, unlike the bare ones which deflated due to the liquefaction of hydrogen. (b) Biaxial strain versus T for a MoS_2 bubble before (full squares) and after hBN-capping (empty squares). The grey area indicates the temperature range in which the hydrogen in the bubble is in a liquid state and the bare bubble is deflated. (c) μ-PL spectrum of a hBN-capped WS_2 bubble taken at 6.8 K with excitation power of 20 μW. The lone quantum emitter is labelled δ. The white dashed lines in the inset indicates the bubble position; the area excited by the laser is at itse edge. (d) Second-order autocorrelation function $g^{(2)}(\tau)$ relative to emitter δ. Its value at $\tau = 0$ is 0.183 ± 0.069, well below 0.5. (e) Zeeman splitting ΔE versus magnetic field B relative to a SPE, labelled α, observed in a bubble. From eq. (1) a g-factor equal to -8.034 ± 0.054 is found. Reproduced with permission from Cianci S. *et al.*, *Adv. Opt. Mater.*, **11** (2023) 2202953. Copyright 2023 the authors.

at cryogenic temperatures. The method to create such structures was pioneered by our research team and it consists in irradiating bulk flakes of TMD crystals with low-energy protons: the protons penetrate through the first layer of the crystals and H_2 molecules form (with electrons coming from the ground contact). The H_2 gas coalesces and lifts the topmost layer of the crystal up to forming bubble-shaped structures [5].

These structures, however, deflate when approaching cryogenic temperatures, since hydrogen liquefies at around 32 K, hindering their utilisation for quantum photonics. Remarkably, we found out that the deflation process can be avoided by capping the bubbles with few-layer-thick hBN (see fig. 1(a)). Raman measurements of the hBN-capped structures allowed us to characterise their strain, and optical studies at cryogenic temperature led to the observation of SPEs originating from localised excitons [6].

2. – Bubble characterisation and quantum emitters - results and discussion

First, we characterised the strain amount of MoS_2 and hBN/MoS_2 bubbles with respect to temperature through Raman measurements. The measurements were performed at the bubble centre, *i.e.*, where strain is maximum (and holds a biaxial character) [5,7].

We focused on the study of the E_{2g} modes of the bubbles, which refer to in-plane vibrations because of their particular sensitivity to the applied strain symmetry [8]. Given that the E_{2g} Raman mode shifts linearly with strain, with a shift rate that is known from previous works [7], it is possible to derive the biaxial strain by an analysis of the frequency of the E_{2g} Raman modes of the bubble itself. Raman spectra and details on the calculation of strain are provided in ref. [6], while a summary of the strain values obtained for a MoS_2 bubble before and adter hBN-capping is provided in fig. 1(b). The strain of the bare bubble decreases with decreasing temperature from a value of $\sim 2\%$ at room-temperature (RT) to $\sim 1\%$ at ~ 30 K due to its gradual size shrinkage. Below about ~ 30 K, the bubble deflates and the monolayer sticks to the bulk flake underneath. On the other hand, in the hBN-capped bubble, the biaxial strain remains almost constant at $\sim 1.6\%$ in the 5 K - RT range [6]. This strain is much higher than that typically achieved at cryogenic tempertures [8].

We thus investigated the potentiality of the system for quantum emission by looking for evidence of SPEs in the μ-PL spectra of an ordered array of hBN-capped WS_2 bubbles at about 7 K. We focused our attention on WS_2 structures because this material is characterised by an intense PL emission and since SPEs in WS_2 were achieved only in a few studies (most of the literature being focused on WSe_2). The ordered array of bubbles was obtained by applying a H-opaque mask with regularly spaced circular holes on the starting bulk WS_2 crystal before the hydrogenation process: the bubbles thus formed only within the circular holes. In the PL spectra, we identified several peaks likely linked to SPEs, mostly around the edges of slightly misshapen bubbles, and performed second-order autocorrelation measurements to confirm their nature as quantum emitters (see fig. 1(c)-(d)). We also performed time-resolved μ-PL measurements to estimate the decay times of the quantum emitters and found them to be in the order of a few ns, in line with those found for localised states in WSe_2 MLs [1, 2, 9]. As we know from previous studies [10, 11], hydrogen-filled TMD micro-bubbles present a strain-induced exciton transition from a direct, near the edges, to an indirect regime, on top of the bubbles. This could explain our observation of quantum emitters just around the edges of the bubbles, where a direct optical transition is found (leading to an intense PL signal) and where the strain is large enough to induce the formation of SPEs. The latter were instead not observed at the bubble centre, where the strain is the largest but the PL signal is significantly less intense due to the indirect nature of the exciton transition.

Finally, we performed magneto-μ-PL measurements at cryogenic temperatures to estimate the gyromagnetic- (g-) factor of the SPEs. We applied magnetic fields up to 12 T and detected light with opposite helicity through polarisation-resolved measurements. We determined the energy (E) of the left circularly (σ^+) and right circularly (σ^-) polarised PL emission of the SPEs and estimated the Zeeman splitting as $\Delta E(B) = E(\sigma^+) - E(\sigma^-)$. In turn, the exciton g-factor can be derived from the formula

$$\Delta E = \mu_B g B, \quad (1)$$

where μ_B is the Bohr magneton. See fig. 1(e) for the analysis of the g-factor of a SPE found in a hBN/WS_2 dome. A statistical analysis of the measured g-factors leads to an average value of -8.20 ± 0.51, roughly twice the value reported for the free exciton in WS_2 MLs [1, 2, 12-14]. Such a value supports the hypothesis that the SPEs originate from defect-localised dark excitons involving a hole in the valence band maximum and an electron in the conduction band minumum (CBM) with opposite spin (a g-factor of about -9 is expected for such exciton [15]). Strain brings the CBM in resonance with defect states, inducing their hybridisation, and, consequently, the dark exciton brightens.

In conclusion, ordered arrays of quantum emitters can be obtained in hBN-capped WS_2 bubbles. The process could be further optimised by a fine tuning of the strain, *e.g.*, by the creation of lithographically defined masks with custom-designed holes. Furthermore, the improvement of the PL emission signal and the decay time of the emitters through the integration of the hBN-capped bubbles within photonic and plasmonic cavities could lead to a surge of interest in TMD-based SPEs for quantum technologies.

* * *

The authors are grateful to A. Polimeni, M. Felici and G. Pettinari for their contribution to the results presented in this work.

REFERENCES

[1] Kumar S., Kaczmarczyk A. and Geradot B. D., *Nano Lett.*, **15** (2015) 7567.
[2] Srivastava A., Sidler M., Allain A. V., Lembke D. S., Kis A. and Imamoğlu A., *Nat. Nanotechnol.*, **10** (2015) 491.
[3] Palacios-Berraquero C., Barbone M., Kara D. M., Chen X., Goykhman I., Yoon D., Ott A. K., Beitner J., Watanabe K., Taniguchi T., Ferrari A. C. and Atatüre M., *Nat. Commun.*, **7** (2016) 12978.
[4] Branny A., Wang G., Kumar S., Robert C., Lassagne B., Marie X., Gerardot B. D. and Urbaszek B., *Appl. Phys. Lett.*, **108** (2016) 142101.
[5] Tedeschi D., Blundo E., Felici M., Pettinari G., Liu B., Yildrim T., Petroni E., Zhang C., Zhu Y., Sennato S., Lu Y. and Polimeni A., *Adv. Mater.*, **31** (2019) 1903795.
[6] Cianci S., Blundo E., Tuzi F., Pettinari G., Olkowska-Pucko K., Parmenopoulou E., Peeters D. B. L., Miriametro A., Taniguchi T., Watanabe K., Babinski A., Molas M. R., Felici M. and Polimeni A., *Adv. Optical Mater.*, **11** (2023) 2202953.
[7] Blundo E., Yildrim T., Pettinari and Polimeni A., *Phys. Rev. Lett.*, **127** (2021) 046101.
[8] Blundo E., Cappelluti E., Felici M., Pettinari G. and Polimeni A., *Appl. Phys. Rev.*, **8** (2021) 021318.
[9] Luo Y., Shepard G. D., Ardelean J. V., Rhodes D. A., Kim B., Barmak K., Hone J. C. and Strauf S., *Nat. Nanotechnol.*, **13** (2018) 1137.
[10] Blundo E., Felici M., Yildirim T., Pettinari G., Tedeschi D., Miriametro A., Liu B., Ma W., Lu Y. and Polimeni A., *Phys. Rev. Res.*, **2** (2020) 012024.
[11] Blundo E., Faria P. E. jr., Surrente A., Pettinari G., Prosnikov M., Olkowska-Pucko K., Zollner K., Woźniak T., Chaves A., Kazimierczuk T., Felici M., Babiński A., Molas M. R., Christianen P. M. C., Fabian J. and Polimeni A., *Phys. Rev. Lett.*, **129** (2022) 067402.
[12] Shepard G. D., Ajayi O. A., Li X., Zhu X.-Y., Hone J. and Strauf S., *2D Mater.*, **4** (2017) 021019.
[13] Dang J., Sun S., Xie X., Yu Y., Peng K., Qian C., Wu S., Song F., Yang J., Xiao S., Yang L., Wang Y., Rafiq M. A., Wang C. and Xu X., *npj 2D Mater. Appl.*, **4** (2020) 2.
[14] Stier A. V., McCreary K. M., Jonker B. T., Kono J. and Crooker S. A., *Nat. Commun.*, **7** (2016) 10643.
[15] Wozniak T, Faria P. E. jr., Seifert G., Chaves A. and Kunstmann J., *Phys. Rev. B*, **23** (2020) 235408.