Patterned tungsten disulfide/graphene heterostructures for efficient multifunctional optoelectronic devices†

A. Rossi, †a,b D. Spirito, †c F. Bianco, †b S. Forti, †d F. Fabbri, †a H. Büch, †a C. Tredicucci, †b,d R. Krahne †c,e and C. Coletti †a,e

In the last decade van der Waals (vdW) materials have been in the spotlight of the scientific community, since their two-dimensional (2d) nature allows the direct exploration of electronically confined systems.† Graphene has been so far the most investigated 2d material and has proven to be a table top quantum electronic system, despite sharing the same vdW 2d nature.4,5 The combination of these two 2d materials has paved the way for a variety of device concepts.6 Among TMDs, one of the most investigated 2d material and has proven to be a versatile multifunctional material that still has to be efficiently addressed is that of tungsten disulfide (WS₂). In its monolayer form, it shows a direct bandgap of 2.1 eV at the two non-equivalent K-points of the Brillouin zone.7 In the vicinity of those points it shows a remarkable splitting of the valence band due to spin-orbit coupling.8,9 Because of symmetry selection rules, spin polarized carriers can be promoted in the conduction band using polarized light.7,10,11 Its optical properties can be used for photodetection to enhance the response of graphene. Indeed, when placed in vertical heterostacks,12 the charge transfer between WS₂ and graphene under optical pumping13 was reported to be fast and efficient. Recently, much effort has been devoted to create efficient hybrid TMD/graphene photodetectors.12,14,15 Room temperature photoresponsivities as high as R ~ 5 × 10⁸ A W⁻¹ 16 and very fast response times (down to τ = 130 µs)17 have been demonstrated. Yet, one major issue that still has to be efficiently addressed is that of device scalability. Indeed, hybrid photodetectors are generally fabricated using exfoliated TMD/graphene heterostructures. Very recently, photodetectors obtained by combining one layer produced by chemical vapor deposition (CVD) with exfoliated flakes have been reported,17 but although performing well they lack in scalability. Devices fabricated with heterostacks obtained only with CVD grown materials have also been recently proposed.18–20

In this work, we report an original approach for the fabrication of efficient optoelectronic devices from scalable tungsten disulfide (WS₂)/graphene heterostructures. Our approach allows for the patterned growth of WS₂ on graphene and facilitates the realization of ohmic contacts. Photodetectors fabricated with WS₂ on epitaxial graphene on silicon carbide (SiC) present, when illuminated with red light, a maximum responsivity R ∼220 A W⁻¹, a detectivity D* ∼2.0 × 10⁹ Jones and a −3 dB bandwidth of 250 Hz. The retrieved detectivity is 3 orders of magnitude higher than that obtained with graphene-only devices at the same wavelength. For shorter illumination wavelengths we observe a persistent photocurrent with a nearly complete charge retention, which originates from deep trap levels in the SiC substrate. This work ultimately demonstrates that WS₂/graphene optoelectronic devices with promising performances can be obtained in a scalable manner. Furthermore, by combining wavelength-selective memory, enhanced responsivity and fast detection, this system is of interest for the implementation of 2d-based data storage devices.
possibility to transfer the heterostack on a selected substrate – either flexible or rigid – and a high photoresponsivity up to hundreds of A W$^{-1}$. However, despite being a large-scale approach, its extension to wafer-scale is complicated by the transfer step.

A possible solution to the abovementioned hurdles has been recently reported in our previous work through the demonstration of the direct scalable synthesis via CVD of continuous mono-bilayer WS$_2$ on epitaxial graphene (EG) on silicon carbide (SiC). The WS$_2$ layer synthesized in this way is azimuthally aligned with the underlying EG. The precise band alignment and the atomically sharp interfaces of this heterostack are crucial to control the optoelectronic properties of the full structure. In this work, we demonstrate an entirely scalable hybrid WS$_2$/EG photodetector with a maximum photoresponsivity $R \sim 220$ A W$^{-1}$ under continuous-wave illumination and a $-3$ dB bandwidth of 250 Hz. The photodetectors also display wavelength-dependent persistent photoconductivity (PPC). The devices were realized with a novel approach for the patterned growth of WS$_2$ on EG, so that WS$_2$ is present only in the active areas for photodetection and the underneath graphene is accessible to metal deposition of ohmic contacts.

Indeed, contacting the WS$_2$ directly would generate a Schottky barrier. This approach allows minimizing the contact resistance and thus improving the photodetection efficiency.

Methods

Synthesis and patterned masking of graphene

EG was grown on nominally on-axis high purity semi-insulating (HPSI) 4H-SiC(0001) substrates (CREE, Inc.) by adapting the approach reported by Emtsev and coworkers in an Aixtron HT-BM reaction chamber. Before proceeding with WS$_2$ growth, the areas of graphene where contacts shall be subsequently deposited were masked by evaporating 100 nm of gold (Au) (Fig. 1(a)). Au is a highly suitable mask material, because it can sustain high temperatures and it is inert to sulfur (S) atmosphere, therefore remaining unaffected during the growth process. The Au mask was obtained using a standard procedure: graphene coating with poly(methyl methacrylate) (PMMA) resist, followed by electron beam lithography (EBL), thermal evaporation of Au and lift-off. It is important to mention that the same results, also in terms of graphene/con-
contacts interface quality, could be achieved using temperature-resistant resist hydrogen silsesquioxane (HSQ) instead of Au mask. This material, once exposed, turns into a film of silicon oxide that can sustain the WS₂ growth conditions as well. After the masking phase it can be etched using a 1 : 5 HF : H₂O solution. HSQ offers an alternative to the expensive Au (i.e., for sustaining the high growth temperatures at least 100 nanometers of Au need to be evaporated). The choice of the mask can be dictated by the resistance of the substrate to the mask etchant.

**WS₂ synthesis**

WS₂ was synthesized on partially masked graphene (Fig. 1(b)) using a growth process similar to that reported elsewhere. However, in the present work, the growth recipe was adapted in order to obtain a continuous WS₂ monolayer film. Sulfurization of tungsten trioxide (WO₃) powder (Sigma Aldrich, 99.995%) was carried out in a horizontal hot-wall furnace (Lenton PTF). The growth temperature within the hot-zone was set to 920 °C and the growth time was 1 h. The EG substrate was placed face-up next to the WO₃ powder and within the same crucible. Argon (Ar) was flown during the temperature ramp with a flux of 500 sccm, leading to a pressure of 4.5 mbar, which kept the S solid. After reaching 920 °C, the Ar flux was suddenly reduced to 8 sccm, which reduced the furnace pressure to 0.5 mbar, triggering S evaporation. In order to obtain sudden S evaporation, chalcogen crystals were heated up at 200 °C by wrapping a heating belt around the quartz tube.

**Device fabrication**

After the growth of WS₂, some 2d crystals were deposited also on the Au mask (Fig. 1(c)). Removing these crystals before removing the mask is a crucial step to ensure a clean interface with the bare graphene. Therefore, the top surface of the mask was exposed to reactive ion etching with O₂ and Ar plasma while protecting the active area by PMMA layer. After a cleaning in acetone, the sample was immersed in a solution of potassium iodide for 3 minutes (H₂O : KI : I₂ in ratio 40 : 4 : 1) in order to remove the Au mask. This allowed for the creation of well-defined channels (Fig. 1(d)) with width of 30 µm and lengths of 2, 5 and 10 µm (device areas 60, 150 and 300 µm², respectively). If not differently specified, the results reported are relative to devices with shorter channel length, namely 2 µm. Once the WS₂/graphene channels were defined, ohmic contacts (source and drain) were fabricated via standard EBL, followed by metal deposition (Ti/Au 10/80 nm) and lift-off (Fig. 1(e)).

**Raman and photocurrent measurements**

Raman characterization of the synthetized films was carried out with a commercial Renishaw inVia system equipped with a 532 nm green laser. Photocurrent measurements were performed at room temperature in a vacuum probe station from Janis Research (~2 × 10⁻¹⁵ mbar). A bias voltage between source and drain contacts was applied up to 2 V. Illumination was provided through an optical window using laser diodes coupled into a fiber and focused on the sample in a spot size of approximately 1 mm, aligned on the devices with micrometer controlled stages. The devices were illuminated with blue (473 nm, 2.62 eV), green (520 nm, 2.38 eV) and red (638 nm, 1.94 eV) lasers. A mechanical shutter was used to block the light passing through the window for dark measurements. Before measuring the photoresponse, current-voltage (IV) characterization in the dark was performed. The photoresponsivity was assessed for photoexcitation intensities ranging from 16 to 680 mW cm⁻² both with continuous and temporally modulated light, referred in the following text as DC and AC, respectively. For DC measurements, a Keithley 2600 SMU was used. For AC measurements, the laser light was modulated either by a chopper or by modulating the drive current of the laser diode. The current was measured through a current amplifier, whose output was measured by a lock-in amplifier locked to the modulation signal. Amplification factors, filters and integration times in the amplifiers were tuned according to the frequency and the noise level of the signal. Further photocurrent measurements were also carried out at a wavelength of 532 nm with the Renishaw inVia system used for Raman characterization in order to ensure an illuminating spot size (variable between 1 µm and 15 µm) that is smaller than the device area. A Keithley 2614B SMU was used for current measurements.

**Results and discussion**

The process flow of our fabrication method is depicted in (Fig. 1(a–e)) while the cross section of the measured devices is reported in panel (f). The quality of graphene outside the channels was assessed via Raman spectroscopy prior to contact deposition (Fig. 1(g–i)). Panel (h) and (i) report representatives spectra measured inside and outside the channel, respectively. In the channel, the photoluminescence (PL) of WS₂ (Fig. 1(h)) is clearly visible and overlapping the Raman signal of graphene (Fig. 1(i)). No appreciable D peak is retrieved and 2D peak position and full width at half maximum (FWHM) are entirely comparable to those of the as-grown material. This confirms that the graphene quality is not affected by the processing. Raman and PL spectra of graphene and WS₂ as-grown and after processing steps are reported in ESI (Fig. S1†). A Raman map of the main peaks of WS₂ – whose position and intensities are indicative of monobilayer – is shown in ESI (Fig. S2†). In Fig. S3, an AFM image of the patterned area prior to contact deposition is reported, showing a flat graphene surface conforming with the WS₂/graphene device area. Our fabrication approach allows for the implementation of regular device arrays, as demonstrated in the optical microscope image (Fig. 1(l)). The electrical characterization of the device is reported in Fig. S4† and confirms the ohmic behavior of the graphene-Ti/Au contacts. The effective resistivity, extracted from transfer length measurements (TLM) reported in Fig. S5, is (1.35 ± 0.08) × 10⁴ Ω μm, which is typical for this kind of samples. Both the AFM ana-
To the best of our knowledge, this response time is among the fastest obtained for TMD/graphene devices. It is worth of note that a significant signal can be detected also above 10 kHz, where the responsivity is \( \sim 10\% \) of the maximum value. We believe that the clean ohmic contact obtained with our approach is at the basis of the fast response time of our devices. Furthermore the epitaxial relation in our heterostack could have a positive impact as well.

In Fig. 3 the wavelength-dependent behavior of the device is reported. Fig. 3(a) shows the WS2/graphene device responsivity in AC at 173 Hz, for three different illumination wavelengths. The responsivities, within the error bars, are generally unaffected by the change in wavelength and, overall, responsivity decreases with increasing light intensity.

Fig. 3(b) reports the temporal response of the photocurrent under DC illumination at different wavelengths for on/off cycles with period of 20 s. The three curves collected at different wavelengths are offset on the vertical axis for sake of clarity. In this case, the response changes dramatically when we switch from blue (473 nm) to red (638 nm) light. With the excitation at 473 nm once the light is switched off, there is a PPC that remains even on a time scale of hours (see ESI Fig. S6(a)†). The PPC is observed (although to a lesser extent) also for the green illumination, while for excitation with the
measured temporal response of the photocurrent, we analyze the illuminated area of the device. Before discussing in detail the restored. The observed finite decay is attributed to the smaller after several minutes the dark condition of the device is kept accumulating when increasing the power at each cycle. As can be seen in the photogating behavior (see ESI, Fig. S7†).

Graphene-only devices displayed the same PPC observed for the WS2/graphene devices (see ESI Fig. S6(b)†). Hence, the observed PPC – differently from what reported in ref. 16 – is not an intrinsic property of the hybrid heterostack. In order to understand the mechanism behind the PPC, the temporal response has been measured when illuminating the WS2/graphene 2 µm device with a spot diameter larger than the channel length, but smaller than the channel width (diameter 15 µm, 532 nm laser). The illumination was switched off only when approaching current saturation. As can be seen in Fig. 4(a), the device shows a slowly decaying “off” current, but after several minutes the dark condition of the device is restored. The observed finite decay is attributed to the smaller illuminated area of the device. Before discussing in detail the measured temporal response of the photocurrent, we analyze the band alignment of our structure, i.e. of the WS2 on epitaxial graphene on 4H-SiC, which we have directly measured via angle-resolved photoemission spectroscopy (ARPES).32 The properties reported in ref. 9 are valid for the case investigated in this work, since the doping level of the epitaxial graphene on hexagonal SiC(0001) is not influenced by the polytype (i.e., 4H or 6H).32 Furthermore, assuming that the HPSI 4H-SiC used as a substrate has the chemical potential at midgap, the total band alignment is the one sketched in Fig. 4(b). The energy band diagram of 4H-SiC is reported on the left, while the graphene cone, schematized in the center, presents the Dirac point 0.4 eV below the Fermi level, a hallmark for EG.33,34 On the right-hand side of panel (b), WS2 bands are reported with the conduction band lying about 260 meV above the Fermi level, as reported for the WS2/EG system.9 HPSI 4H-SiC displays several deep levels (sketched in panel b) with activation energies ranging between 0.7 eV and 0.9 eV below the SiC conduction band,35 which are known to play a fundamental role in the semi insulating behavior of 4H-SiC. These intrinsic deep levels are either acceptor-like levels or negative-U centers generated from C-vacancy complexes (e.g., Z1/2 levels), and act as recombination centers and lifetime killers in charge transport experiment.36–38 These defects in the 4H-SiC substrate are responsible for the photogating mechanism in our devices, preventing the decay of the photocurrent. As depicted in Fig. 4(c), if the impinging light has enough energy (i.e. larger than ~2.2 eV corresponding to a wavelength shorter than 563 nm), it is not only responsible for photocurrent in the WS2/graphene heterostructure, but it also promotes electrons into the aforementioned 4H-SiC deep levels. By acting as recombination centres, such levels capture and neutralize electrons and leave charged holes behind. The accumulated holes generate an electric field that leads to a chemical potential shift in graphene, increasing the number of carriers (Fig. 4(d)). Since the trapping lifetime of these defects is extremely long,39 PPC is observed. Nevertheless, eventually they recombine (Fig. 4(e)), thus the related gate voltage decays and the initial position of the chemical potential is restored. The presence of defect levels with different activation energies is responsible for the distinct behavior observed for blue and green light, e.g. when Z1/2 deep levels are involved, a PPC lasting for several hours is obtained. Red light does not induce any long-lifetime deep level transition,40 and therefore no photogating and no
PPC occur. However, the energy of the red light is sufficient to excite the transition from VB to CB in WS$_2$. Subsequently, charge transfer from the active layer (WS$_2$) to graphene occurs, injecting carriers in the transport layer (graphene). Hence, the role of WS$_2$ is crucial to enhance the responsivity of the system making the device “active” in the visible range.

**Conclusion**

We reported a novel approach for the implementation of scalable WS$_2$/graphene photoresponsive devices. The use of a mask during the growth is crucial to controllably deposit WS$_2$ just on the optical channel in order to create an effective ohmic contact to the graphene channel. The strength of this approach relies on its flexibility as it can be adopted on different systems, e.g. CVD graphene transferred on SiO$_2$. The presented devices show – when illuminated with red light – a DC responsivity reaching 220 A W$^{-1}$ and an AC response time of $\tau_r \sim 0.6$ ms. PPC is measured for shorter illumination wavelengths, and a nearly perfect charge retention is observed for blue light. Such PPC originates from deep levels in the SiC substrate. The combination of wavelength-selective memory effect, enhanced responsivity and fast detection is of interest for the fabrication of 2d based optical memories, which might be realized by exploiting a transparent top gate$^{17}$ to reset the memory state and depopulate the traps.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

The authors would like to thank Mirko Rocci from NEST-Scuola Normale Superiore, for fruitful discussion. The research leading to these results has received funding from the European Union’s Horizon 2020 research and innovation program under Grant agreement No. 696656 – GrapheneCore1, and under the Marie Sklodowska-Curie Grant Agreement COMPASS No. 691185.

**References**

1. A. Kuc, N. Zibouche and T. Heine, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, 83(24), 245213.
2. M. I. Katsnelson, K. S. Novoselov and A. K. Geim, *Nat. Phys.*, 2006, 2(9), 620–625.
3. K. S. Novoselov, V. I. Fal’ko, L. Colombo, P. R. Gellert, M. G. Schwab and K. Kim, *Nature*, 2012, 490, 192–200.
4. M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh and H. Zhang, *Nat. Chem.*, 2013, 5(4), 263–275.
5 Q. Hua Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman and M. S. Strano, *Nat. Nanotechnol.*, 2012, 7, 699–712.
6 A. K. Geim and I. V. Grigorieva, *Nature*, 2014, 499(7459), 419–425.
7 X. Xu, W. Yao, D. Xiao and T. F. Heinz, *Nat. Phys.*, 2014, 10(3), 343–350.
8 M. Dendzik, M. Michiardi, C. Sanders, M. Bianchi, J. A. Miwa, S. S. Gronborg, J. V. Lauritsen, A. Bruix, B. Hammer and P. Hofmann, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2015, 92(24), 245442.
9 S. Forti, A. Rossi, H. Büch, T. Cavallucci, F. Bisio, A. Sala, T. O. Menteš, A. Locatelli, M. Magnuzzo, M. Canepa, K. Müller, S. Link, U. Starke, V. Tozzini and C. Coletti, *Nanoscale*, 2017, 9(42), 16142–16149.
10 P. K. Nayak, F. C. Lin, C. H. Yeh, J. S. Huang and P. W. Chiu, *Nanoscale*, 2016, 8(11), 6035–6042.
11 A. Rossi, H. Büch, C. Di Rienzo, V. Miseikis, D. Convertino, A. Al-Temimy, V. Voliani, M. Gemmi, V. Piazza and C. Coletti, *2D Mater.*, 2016, 3(3), 31013.
12 F. H. L. Koppens, T. Mueller, P. Avouris, A. C. Ferrari, M. S. Vitiello and M. Polini, *Nat. Nanotechnol.*, 2014, 9(10), 780–793.
13 J. He, N. Kumar, M. Z. Bellus, H.-Y. Chiu, D. He, Y. Wang and H. Zhao, *Nat. Commun.*, 2014, 5, 5622.
14 M. Buscema, J. O. Island, D. J. Groenendijk, S. I. Blanter, G. A. Steele, H. S. van der Zant and A. Castellanos-Gomez, *Chem. Soc. Rev.*, 2015, 44(11), 3691–3718.
15 C. Xie, C. Mak, X. Tao and F. Yan, *Adv. Funct. Mater.*, 2017, 27(19), 1603886.
16 K. Roy, M. Padmanabhan, S. Goswami, T. P. Sai, G. Ramalingam, S. Raghavan and A. Ghosh, *Nat. Nanotechnol.*, 2013, 8(11), 826–830.
17 J. D. Mehew, S. Unal, E. Torres Alonso, G. F. Jones, S. Fadhil Ramadhan, M. F. Craciun and S. Russo, *Adv. Mater.*, 2017, 1700222, 1700222.
18 H. Tan, Y. Fan, Y. Zhou, Q. Chen, W. Xu and J. H. Warner, *ACS Nano*, 2016, 10, 7866–7873.
19 C. Lan, C. Li, S. Wang, T. He, Z. Zhou, D. Wei, H. Guo, H. Yang, Y. Liu and R. Wallace, *J. Mater. Chem. C*, 2017, 5(6), 1494–1500.
20 D. De Fazio, I. Goykhman, D. Yoon, M. Bruna, A. Eiden, S. Milana, U. Sassì, M. Barbone, D. Duncenco, K. Marinov, A. Kis and A. C. Ferrari, *ACS Nano*, 2016, 10(9), 8252–8262.
21 D. Ovchinnikov, A. Allain, Y.-S. Huang, D. Duncenco and A. C. Ferrari, *ACS Nano*, 2014, 8(7), 8174–8181.
22 N. Perea-López, Z. Lin, N. R. Pradhan, A. Iñiguez-Rábago, A. Laura Elias, A. McCreary, J. Lou, P. M. Ajayan, H. Terrones, L. Balicas and M. Terrones, *2D Mater.*, 2014, 1(1), 11004.
23 K. V. Emstev, A. Bostwick, K. Horn, J. Jobst, G. L. Kellogg, L. Ley, J. L. Mcchesney, T. Ohta, S. A. Reshanov, J. Röhrle, E. Rotenberg, A. K. Schmid, D. Waldmann, H. B. Weber and T. Seyller, *Nat. Mater.*, 2009, 8, 203–207.
24 J.-H. Kang, Y. Ronen, Y. Cohen, D. Convertino, A. Rossi, C. Coletti, S. Heun, L. Sorba, P. Kacman and H. Shtrikman, *Semicond. Sci. Technol.*, 2016, 31(11), 115005.
25 Y. Gao, Z. Liu, D.-M. Sun, L. Huang, L.-P. Ma, L.-C. Yin, T. Ma, Z. Zhang, X.-L. Ma, L.-M. Peng, H.-M. Cheng and W. Ren, *Nat. Commun.*, 2015, 6, 8569.
26 S. Fiori, Y. Murata, S. Veronesi, A. Rossi, C. Coletti and S. Heun, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2017, 96(125429), 1–8.
27 W. Zhao, Z. Ghorannevis, K. K. Amara, J. R. Pang, M. Toh, X. Zhang, C. Kloc, P. H. Tan and G. Eda, *Nanoscale*, 2013, 5(20), 9677.
28 A. Berkdemir, H. R. Gutiérrez, A. R. Botello-Méndez, N. Perea-López, A. L. Elias, C.-I. Chia, B. Wang, V. H. Crespi, F. López-Urías, J.-C. Charlier, H. Terrones and M. Terrones, *Sci. Rep.*, 2013, 3, 183–191.
29 V. K. Nagareddy, I. P. Nikitina, D. K. Gaskill, J. L. Tedesco, R. L. Myers-Ward, C. R. Eddy, J. P. Goss, N. G. Wright and A. B. Horsfall, *Appl. Phys. Lett.*, 2011, 99(7), 73506.
30 M. Kato, S. Tanaka, M. Ichimura, A. Aral, S. Nakamura, T. Kimoto and R. Plasser, *J. Appl. Phys.*, 2006, 100(5), 53708.
31 G. Konstantatos, I. Howard, A. Fischer, S. Hoogland, J. Clifford, E. Klem, L. Levine and E. H. Sargent, *Nature*, 2006, 442(7099), 180–183.
32 J. Ristein, S. Mammadov and T. Seyller, *Phys. Rev. Lett.*, 2012, 108(24), 246104, 1–5.
33 A. Bostwick, T. Ohta, T. Seyller, K. Horn and E. Rotenberg, *Nat. Phys.*, 2007, 3(1), 36–40.
34 K. V. Emstev, F. Speck, T. Seyller, L. Ley and J. D. Riley, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, 77(15), 155303.
35 T. Dalibor, G. Penski, H. Matsunami, T. Kimoto, W. J. Choyke, A. Schönert and N. Nordell, *Phys. Status Solidi A*, 1997, 162(1), 199–225.
36 N. T. Son, X. T. Trinh, L. S. Lovlie, B. G. Svensson, K. Kawahara, J. Suda, T. Kimoto, T. Umeda, J. Isoya, T. Makino, T. Ohshima and E. Janzén, *Phys. Rev. Lett.*, 2012, 109(18), 23–27.
37 K. Kawahara, X. T. Trinh, N. T. Son, E. Janzén, J. Suda and T. Kimoto, *Appl. Phys. Lett.*, 2013, 102(11), 112106.
38 K. Kawahara, X. T. Trinh, N. T. Son, E. Janzén, J. Suda and T. Kimoto, *J. Appl. Phys.*, 2014, 115(143705), 2–8.
39 E. N. Kalabukhova, S. N. Lukin, D. V. Savchenko, A. A. Sitnikov, W. C. Mitchel and S. Greulich-Weber, *Mater. Sci. Forum*, 2006, 527–529, 563–566.
40 E. N. Kalabukhova, S. N. Lukin, D. V. Savchenko, W. C. Mitchel and W. D. Mitchell, *Mater. Sci. Forum*, 2004, 457–460, 501–504.