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β-Ga_2O_3 nanowires for an ultraviolet light selective frequency photodetector

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Abstract
The behaviour of β-Ga_2O_3 nanowires as photoconductive material in deep ultraviolet photodetectors to operate in the energy range 3.0–6.2 eV has been investigated. The nanowires were grown by a catalyst-free thermal evaporation method on gallium oxide substrates. Photocurrent measurements have been carried out on both undoped and Sn-doped Ga_2O_3 nanowires to evidence the influence of the dopant on the photodetector performances. The responsivity spectrum of single nanowires show maxima in the energy range 4.8–5.4 eV and a strong dependence on the pulse frequency of the excitation light has been observed for undoped nanowires. Our results show that the responsivity of β-Ga_2O_3 nanowires can be controlled by tuning the chopper frequency of the excitation light and/or by doping of the nanowires. Non-linear behaviour in characteristic current–voltage curves has been observed for Ga_2O_3 : Sn nanowires. The mechanism leading to this behaviour has been discussed and related to space-charged-limited current effects. In addition, the responsivity achieved by doped nanowires at lower bias is higher than for undoped ones.

Keywords: photocurrent, nanowire, gallium oxide

(Some figures may appear in colour only in the online journal)

1. Introduction

One-dimensional nano- and microstructures of transparent conductive oxides (TCO) are a subject of increasing interest. Their physical properties, such as luminescence, wave-guiding, field emission and electrical photoresponse, have potential applications in optoelectronic and sensing devices [1–3]. In particular, recent works have demonstrated the feasibility of solar-blind photodetectors using semiconductor oxides, such as ZnO, Zn_2GeO_4 or SnO_2 as photoconductive active materials [4–6]. One of the main criteria in the material choice is the requirement of a wide band gap material, which shows certain electrical conductivity. The goal is to achieve a significant increase in the electrical conductivity during ultraviolet (UV) illumination, while keeping optical transparency in the visible range. Some of the problems of the photoconductive detectors, in comparison with other types of photodetectors involving p–n junctions, are the higher dark current and the longer recovery process. To overcome these drawbacks, oxide semiconductor nanostructures have been proposed as effective UV detectors because of two main factors related to their high surface-to-volume ratio: (i) the presence of hole-state traps at the nanowire surface, that enhance carrier lifetime, and (ii) a shorter transit time in nanowires than in thin films due to the small size of nanowires [4]. Among binary TCOs, monoclinic gallium oxide (β-Ga_2O_3) is a good candidate for this purpose as it exhibits: one of the widest energy band gaps, $\sim$4.9 eV, chemical and thermal stability and low carrier concentration under dark conditions at room temperature [7]. The n-type electrical conduction of undoped β-Ga_2O_3 has been related to shallow donor centres associated to oxygen vacancies and/or external impurities [8–10]. Some applications exploiting the optical and electrical properties of gallium oxide nanowires have been reported, such as gas sensor [11], transparent electronic devices [12], UV photodetectors [13] and waveguides [14–16]. However, there are few works

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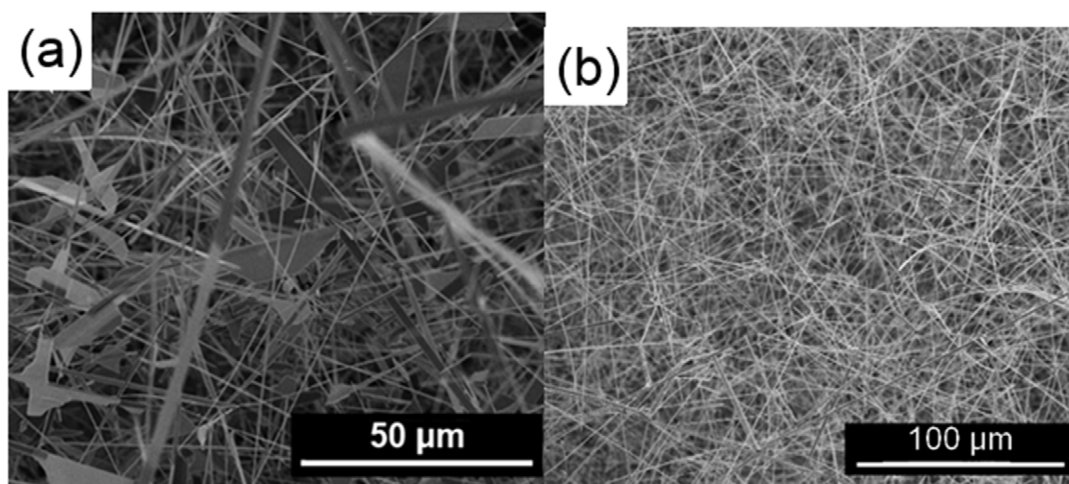

Figure 1. SEM image of the (*a*) undoped and (*b*) Sn-doped Ga_2O_3 nanowires grown on the gallium oxide substrate.

concerning the photoresponse in the deep UV range of Ga_2O_3 nanowires [7, 17, 18].

In this work, we report the response of single undoped and Sn-doped β-Ga_2O_3 nanowires under dynamic excitation conditions with UV photons (3.0–6.2 eV). The illumination source was chopped at frequencies ranging from 16 to 325 Hz. A selective photoresponse of the photodetector, as a function of the chopping frequency has been studied for the undoped case. The mechanisms involved in the photocurrent (PC) process are discussed. The results suggest that the chopped frequency of the excitation light would be a valid parameter to tune the maxima energies in the responsivity curves. On the other hand, a responsivity enhancement is observed for the Sn-doped Ga_2O_3 nanowires.

2. Experimental method

Ga_2O_3 nanowires have been grown by a thermal evaporation method on substrates of compacted gallium oxide pellets, as described in [19]. The pellets were discs of 7 mm diameter and 2 mm thickness and were made by compacting 99.999% purity Ga_2O_3 powders. A pellet with metallic Ga on its top surface was placed in an alumina boat into a horizontal tubular furnace. The thermal treatment consisted of annealing at 1100 °C under an argon gas flow (0.8 l min^{-1}) for 10 h. The synthesis route was the growth of gallium oxide nanowires by thermal oxidation of metallic gallium that acted as source material, avoiding the use of a catalyst. Sn-doped β-Ga_2O_3 nanowires were grown by a similar procedure, but tin oxide powders were added onto the pellet surface. The thermal treatment followed a two-stage profile of 1 h at 1100 °C and 15 h at 1500 °C. In this case, the oxidation of metallic Ga took place in the presence of SnO_2 powders.

The morphological and size characterization of the nanowires was carried out using two scanning electron microscopes (SEMs), either a FEI Inspect S50 or a PHILIPS 515. The current–voltage (I–V) characteristics were performed with a Keithley 6517 electrometer/higher resistance system and a Keithley 6514 source meter. To obtain the PC measurements, a white light from a Xe lamp, which was mechanically chopped at frequencies ranging from 72 to 325 Hz, was focused onto the entrance slit of a monochromator with the output light focused onto the sample. The light wavelength ranged from 200 to 450 nm (corresponding to the energy range 6.2–2.76 eV). The electrical signal generated in the sample was amplified with a Keithley 428 amplifier and collected with a Stanford research system Model SR830DPS lock-in amplifier. The so obtained PC spectra were corrected taking into account the optical response of the system according to the lamp calibration curve (spectral irradiance of Newport's Xe arc lamps).

3. Results and discussion

Figures 1(*a*) and (*b*) show SEM images of the undoped and Sn-doped Ga_2O_3 nanowires, respectively, obtained as described above. All wires had a high aspect ratio with lengths of hundreds of micrometres and diameters of hundreds of nanometres. Previous works of our group on x-ray powder diffraction (XRD), Raman and transmission electron microscopy (TEM) studies have revealed a high crystalline quality of these nanowires and that their structure and stoichiometry correspond to the monoclinic β-Ga_2O_3 phase [19]. Sn concentration is about 1 at% in the Sn-doped Ga_2O_3 nanowires [19]. For the I–V and PC investigations, the nanowires were gently removed from the substrate and placed onto a special sample holder that is illustrated in figure 2(*a*). Measurements were performed on several single nanowires to achieve statistically reliable results. Figure 2(*b*) shows an optical image of a single nanowire in the holder for PC measurements.

Figure 3 shows the typical I–V characteristic of an undoped Ga_2O_3 nanowire for a distance between the Ag contacts of 500 μm, which exhibits an ohmic behaviour. The measurements were carried out at room temperature, in air and dark conditions. The applied voltage was first increased from −100 to 100 V by steps of 0.02 V at a rate of 1 step s^{-1} and then it was decreased in order to check possible hysteresis effects.

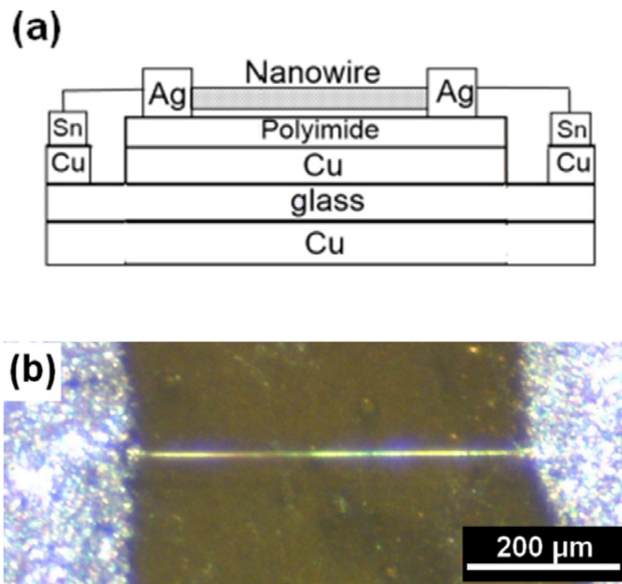

Figure 2. (*a*) Scheme of the sample holder used for PC measurements. (*b*) Optical image of one of the prepared Ga_2O_3 nanowires tested as a photodetector.

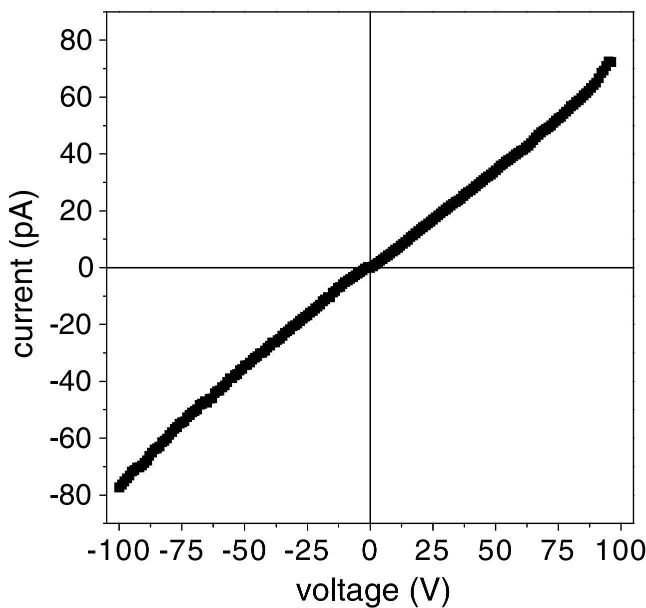

Figure 3. I–V characteristic of a single undoped Ga_2O_3 nanowire obtained in dark and air conditions.

Neither deviation from the ohmic behaviour nor hysteresis effects were observed. The current was found to vary from −80 to 80 pA.

We investigated the responsivity, R_λ, of the undoped Ga_2O_3 nanowire photodetector under UV illumination as a function of the chopper frequency. The responsivity was calculated as the measured PC under unit power density of illumination light. Responsivity curves are drawn in figure 4 for different frequency values. The main bands observed in these spectra, with energies close to the nominal band gap energy of bulk gallium oxide (E_g = 4.9–5.1 eV), have been previously reported by other authors and associated to the absorption edge of β-Ga_2O_3 [20, 21]. These spectra

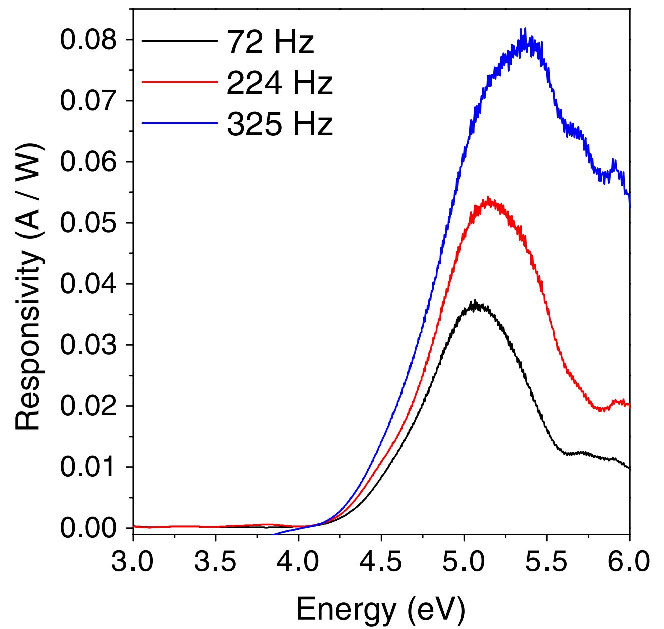

Figure 4. Responsivity spectra for a typical undoped single Ga_2O_3 nanowire obtained at different chopper frequencies. The bias voltage was 500 V.

show a significant UV shift of the band peak and an enhancement of the responsivity as the chopper frequency increases. To explain this result, we consider the possible carriers recombination paths that may control the measured PC. Electrical conduction in Ga_2O_3 is mainly due to the carriers promoted to the conduction band and to the defects band related to oxygen vacancies, which are the responsible for the n-type conductivity in Ga_2O_3 [10, 22]. Characteristic lifetimes of excited carriers in defect related traps in gallium oxide have been found to be around a few milliseconds, while direct band-gap transitions typically have much shorter lifetimes (less than microseconds) [22].

The peak position shift with the chopper frequency could be tentatively assigned to these differences in the lifetimes for different recombination paths. In particular, after excitation at photon energies (E_{ph}) above the band gap, some of the carriers would be trapped at the defect levels within the band gap. This would result in a decrease of the PC signal. When the illumination pulses are sufficiently separated, i.e. at lower chopper frequencies, most of the carriers located in these trapping levels will recombine in the interval between one pulse and the following one. Therefore, the trapping process will be repeated during the following illumination pulse, resulting in a moderate PC. Conversely, for higher chopping frequencies, carriers located at these trapping levels do not have enough time to recombine and the PC increases.

Representative current–voltage (I–V) characteristics for a single Sn-doped Ga_2O_3 nanowire are shown in figure 5. In this case, the distance between Ag contacts was 600 μm. These curves, recorded in air and dark conditions, represent the first (black squares) and the last (red squares) of a series of several I–V scans. The first curve of figure 5(*a*) shows a non-linear I–V characteristic while, after repeated scans, the I–V curve becomes linear as in ohmic behaviour (red

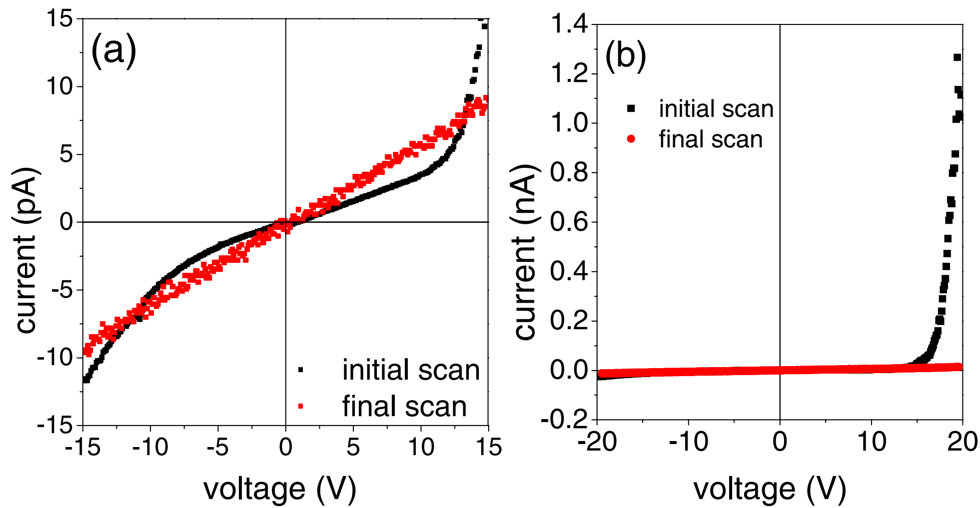

Figure 5. (*a*) I–V characteristics of a single Sn-doped Ga_2O_3 nanowire, showing the I–V characteristics, from −15 to 15 V, after the first scan and after numerous scans. (*b*) I–V characteristic curves of the same nanowire, but from −20 to 20 V.

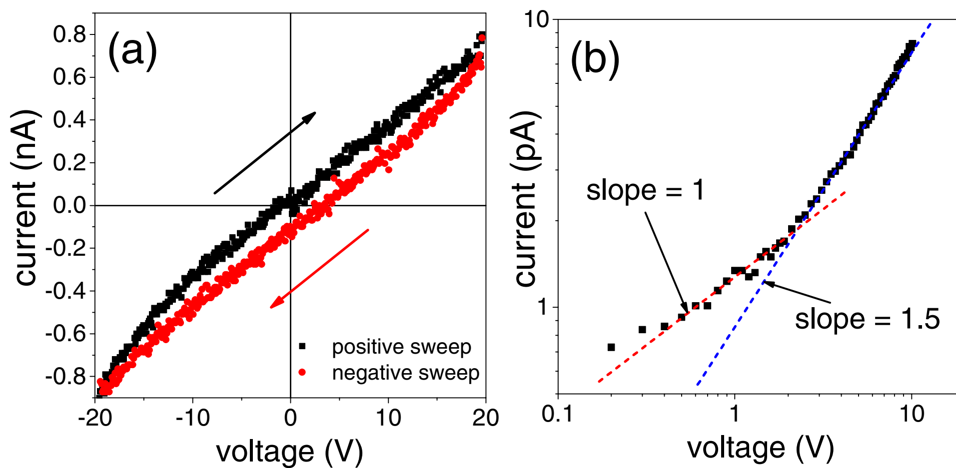

Figure 6. (*a*) I–V hysteresis curve measured with different voltage sweep directions in dark and air conditions and (*b*) I–V (log–log scale) curve of a representative Sn-doped Ga_2O_3 nanowire measured in dark and air conditions during the hysteretic regime.

curve). This evolution of the I–V curves was not observed in the undoped nanowires. In addition, a dramatic increase in the electrical conductivity was observed in the Sn-doped nanowires, as compared with the undoped ones, resulting in current values higher than nanoamperes for bias voltages of 20 V (figure 5(*b*)). This is consistent with other works on Ga_2O_3 nanowires, in which a strong enhancement of the electrical conductivity is observed due to Sn doping [23]. In the transition between the initial, non-linear curve, and the final, linear one, a hysteretic behaviour is also observed, as is shown in figure 6(*a*). This result indicates the existence of an additional charging/discharging current flowing on increase/decrease of the voltage.

The non-linear behaviour is consistent with previous reports on different materials, such as ZnO, GaN or InAs, in which it was associated to space-charged-limited current (SCLC) [24–26]. The SCLC suggests the existence of two conduction regimens. In the former, the behaviour is ohmic ($I \sim V$), while in the latter the current grows with the voltage according to a power law ($I \sim V^{\alpha}$), where α is >1. In order to study this effect, we have recorded I–V curves obtained during the hysteretic regime of one representative Sn-doped nanowire. Figure 6(*b*) shows the I–V curves plotted on a log–log scale, in which two transport regimes are observed: the ohmic behaviour below 2 V, and the trend ($I \sim V^{\alpha}$) with $\alpha \sim 1.5$ for higher voltages. Then, our results confirm that SCLC effects are involved in electrical transport in doped Ga_2O_3 nanowires. On the other hand, the presence of non-linear I–V characteristics in nanowires is often associated to the formation of Schottky barriers at the contacts [12, 27]. However, we have ruled out the influence of the contacts because this effect only appears for Sn-doped wires, demonstrating that this electrical behaviour is due to the nanowire itself and does not depend on the contacts.

Figure 7 plots the responsivity spectrum of a Sn-doped nanowire. This spectrum was obtained by means of a modulated light with a frequency of 236 Hz and a bias voltage of 8 V. Maximum responsivity is 1.2 mA W^{-1} at 8 V bias observed for Sn-doped Ga_2O_3 nanowires. This voltage was used in order to keep the wire in the ohmic region (see figure 5(*a*)). No higher voltages could be used for these measurements as too high currents would have been

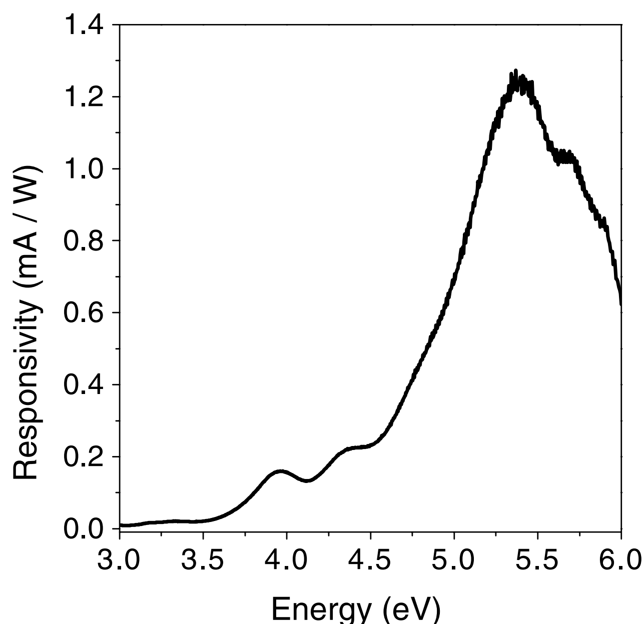

Figure 7. Responsivity spectrum of a single Sn-doped Ga_2O_3 measured at RT and in the air condition. The chopped frequency was 225 Hz and bias voltage was 8 V.

obtained. The comparison of the I–V curves shows that the non-ohmic behaviour of the Sn-doped wires results in a very high increase of the current above and around the 12 V bias, a result we believe to be interesting. On the other hand, for undoped Ga_2O_3, the maximum responsivity is 80 mA W^{-1}. In that case, a voltage equal to 500 V was used because lower voltages resulted in signal/noise ratios too low to reliably measure the PC behaviour. Figure 7 shows that a wide intense band with a peak centred at 5.4 eV and two additional bands centred at 3.9 and 4.4 eV is present in the responsivity spectrum. As discussed above for undoped Ga_2O_3 nanowires, the peaks located at around 4.4 and 5.4 eV may be associated to the photoresponse of the Ga_2O_3 host, while the peak centred at 3.9 eV could be related to the presence of Sn in the wires. Maximenko *et al* [28] calculated the density of states in Ga_2O_3 : Sn, with Sn impurities substituting for Ga^{3+} ions at tetrahedral sites. They ascertained that the energy levels associated to this dopant lie at 0.98 eV below the conduction band minimum, i.e. around 3.9 eV from valence band maximum. On the other hand, Zhang *et al* [29] reported a shoulder around 4.1 eV in the absorption spectra for Sn-doped Ga_2O_3, by increasing the Sn concentration above 10 mol%. Therefore, the 3.9 eV band that we observe in the responsivity curve is in agreement with bands in Ga_2O_3 : Sn associated in previous reports to Sn-related levels.

4. Conclusions

Undoped and Sn-doped β-Ga_2O_3 nanowires were grown by a thermal evaporation method through a catalyst-free vapour–solid process. Current–voltage characteristics of several β-Ga_2O_3 nanowires display an ohmic behaviour, while SCLC behaviour is observed for Sn-doped Ga_2O_3 nanowires. The low resistivity of nanowires makes them suitable for reliable photoconductive photodetectors. Moreover, the photoresponse of an UV photodetector based on single undoped Ga_2O_3 nanowires has been investigated under modulated UV light by a mechanical chopper. By increasing the frequency of the modulated light, the responsivity peak of the UV photodetector has been found to shift from 5.1 to 5.4 eV and an increase of the peak intensity has been observed. The results can be tentatively explained by taking into account the characteristic lifetimes of the localized defect states in gallium oxide. As compared with undoped wires, the photoresponse from Sn-doped wires shows a higher intensity and wider range responsivity at lower bias voltages.

Acknowledgments

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