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Abstract. The absorption and transmission of ZnTe thin films are measured at
wavelengths of 0.32–2.3 μm. The optical constants (n, K) are measured in this
range, although the short wavelength refractive index n measurement is limited by
the band gap. A theoretical calculation of n near the band gap is made from
experimental parameters. An explanation is given for the abnormal decrease of
refractive index near the band gap. The effects of film thickness and doping with
impurities like In, $PbCl_2$, BaF_2 have also been investigated. Effective crystallite size
and strain have been determined by the method of variance analysis of the x-ray
diffraction line profile on the same films. Lattice constants have also been
calculated using the Nelson–Riley plots. It has been observed that there is an
increase in optical band gap with decrease in crystallite size, increase in strain and
decrease in lattice constant value.

1. Introduction

Studies of the structure, galvanomagnetic and optical
properties of ZnTe films have attracted little attention
from the workers in this field, although ZnTe has
potential in γ-ray detectors, solar cells (Parakh 1987),
switching devices (Patel 1986) and as the material for
other optoelectronic studies (Svob *et al* 1986, Vin-
gradov and Vasilevski 1985, Dean 1979). Bulk proper-
ties of ZnTe have been investigated by a number of
workers, and the experimental results obtained have
led to the conclusion that the optical transitions in
ZnTe may be both direct and indirect (Thutupalli and
Tomlin 1976). A model has been proposed by Paw-
likowski (1985) for the determination of absorption
coefficient near the fundamental absorption edge at
normal incidence. From the analysis of absorption
curves different values of direct and indirect band gaps
have been reported by different workers. Thutupalli
and Tomlin (1976) estimated the direct and indirect
band gap of the polycrystalline ZnTe films of 2.23 eV
and 2.56 eV respectively. Mondal *et al* (1987) have
recently reported the dependence of refractive index,
absorption and extinction coefficients on incident pho-
ton energy for ZnTe films deposited on a glass sub-
strate by the hot-wall evaporation technique. But the
dependence of optical constants on the particle size of
the ZnTe films, as well as on nature of doping, has
received limited attention. The present paper reports
the dependence of optical constants on film thickness
and different dopants in ZnTe films deposited on glass
substrates by evaporation. The aim of this investigation
is to study the effect of particle size, RMS strain, lattice
constant, composition and impurities on the optical
band gap and other optical constants.

2. Experimental details

To obtain the thin films, a polycrystalline compound
was synthesised from zinc (99.999%) and tellurium
(99.999%) in an evacuated ($\sim 10^{-4}$ Pa) graphitised (Pal
and Saha 1985) quartz ampoule. The final compound
has been identified to be ZnTe (cubic phase) by x-ray
powder photography. Thin films of ZnTe of different
thickness were deposited on the thoroughly cleaned
glass substrates in a vacuum of the order 10^{-4} Pa keep-
ing the substrates at room temperature and maintaining
the rate of deposition at 120 nm min^{-1}. The com-
position of the deposited films was estimated by EDX
(Camscan Series II with link system). It is observed
that the composition varies with thickness of the films.
The thickness of the films was measured by a stylus
(SF101) as well as by interference. For doping the films
were deposited at 573 K substrate temperature keeping
the deposition parameters the same, and the doping
was done by aftergrowth deposition of the measured
amount of dopants on the surface of the films followed
by a baking at 423 K for six hours with the sample still
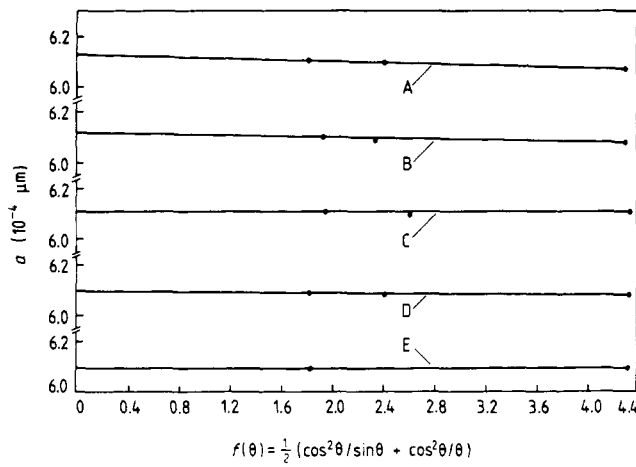under vacuum. With this procedure, indium (6 wt%),

Figure 1. Nelson–Riley plots for ZnTe films: A, a 0.60 μm film deposited at 573 K; B, a 0.80 μm film deposited at room temperature; C, a 0.54 μm film deposited at room temperature; D, a 0.42 μm film deposited at room temperature; E, a 0.27 μm film deposited at room temperature.

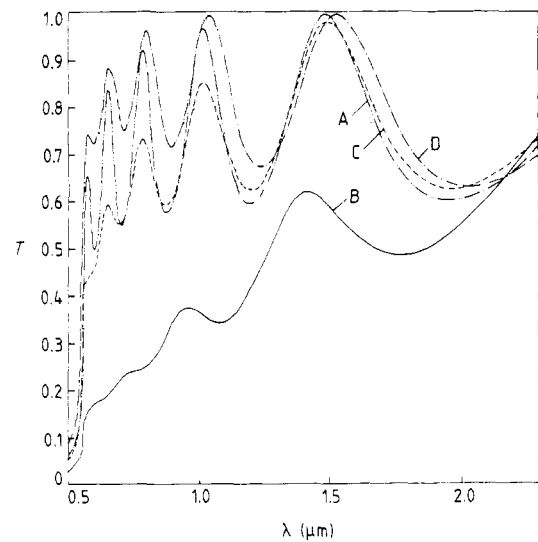**Figure 2.** Transmittance against wavelength: A, —·— undoped ZnTe deposited at 573 K substrate temperature; B, —— ZnTe doped with In (6 wt%); C, – – – ZnTe doped with $PbCl_2$ (6 wt%); D, —··— ZnTe doped with BaF_2 (7 wt%).

lead chloride (6 wt%) and barium fluoride (7 wt%) were doped in ZnTe films. X-ray diffraction patterns of the films of different thickness deposited at room temperature and the films deposited at 573 K were recorded by a Norelco x-ray diffractometer. The particle size and RMS strain were determined from the line broadening of x-ray diffraction patterns by the variance method. Lattice constants of the films deposited at room temperature and at 573 K substrate temperature were determined from their x-ray diffraction patterns, using a Nelson–Riley plot (Nelson and Riley 1945), i.e. of a against $f(\theta)$ (figure 1). We observed that the estimated value of lattice constant for the films deposited at 573 K ($\sim 6.1 \times 10^{-4}$ μm^{-1}) was very close to the bulk value whereas the values were different from those of the bulk value for the films deposited at room temperature (table 1). The absorption and transmission measurements of doped and undoped films were done by a Shimadzu (UV-365) double-monochromator recording spectrophotometer. We observed that the absorption starts with a slow rise in the low-energy region followed by a rapid rise in the higher-energy region.

3. Results and discussion

It has been observed from TEM and the line profile analysis of diffracted x-ray spectrum of ZnTe films

that the films deposited at 573 K substrate temperature which have maximum particle size (150×10^{-4} μm) are those which were grown with the (111) plane parallel to the plane of the substrate (Pal *et al* 1989). The films deposited at that substrate temperature were found to be stoichiometric from EDX data analysis. A similar observation was also reported by Patel and Patel (1983). The transmission curves of doped and undoped films deposited at 573 K substrate temperature are shown in figure 2. The plot of transmission T against wavelength λ is found to vary as (Manifacier *et al* 1976)

$$T = \frac{16 n_a n_g n^2 \exp(-\alpha t)}{R_1^2 + R_2^2 \exp(-2\alpha t) + 2 R_1 R_2 \exp(-\alpha t) \cos(4\pi n t/\lambda)} \quad (1)$$

where

$$R_1 = (n + n_a)(n_g + n)$$

$$R_2 = (n - n_a)(n_g - n).$$

α is the absorption coefficient and n, n_a, n_g are the refractive indices of the film, air and substrate respectively. The maxima and minima in the T–λ plot occur when

$$4\pi n t/\lambda = M\pi \quad (2)$$

Table 1.

Film thickness (μm)	Te/Zn (at.%)	E_g^d (eV)	E_g^i (eV)	Lattice constant, a (μm)	n at $\lambda = 2.0$ μm	Particle size (μm)	RMS strain
0.27	0.852	3.08	2.03	6.090×10^{-4}	2.56	45.7×10^{-4}	394×10^{-4}
0.42	1.016	2.63	1.79	6.097×10^{-4}	2.40	60.0×10^{-4}	304×10^{-4}
0.54	1.132	2.40	1.67	6.109×10^{-4}	2.39	69.0×10^{-4}	220×10^{-4}
0.80	1.321	2.25	1.53	6.121×10^{-4}	2.37	81.0×10^{-4}	250×10^{-4}

where M represents the order number and t is the thickness of the film. The refractive index n may be computed from the relation (Mondal *et al* 1987, Manifacier *et al* 1976, 1977)

$$n^2 = \frac{n_a^2 + n_g^2}{2} + 2n_a n_g T''$$
$$+ \left(\frac{(n_a^2 + n_g^2 + 4n_a n_g T'')^2}{4} - n_a^2 n_g^2 \right)^{1/2} \quad (3)$$

where

$$T'' = \frac{T_{max} - T_{min}}{T_{max} \, T_{min}}.$$

T_{max} and T_{min} represent the envelope of the maxima and minima position of the T–λ curve (figure 2). An exponential variation in T with absorption coefficient α is most probable near the absorption edge, so α may be determined from

$$T = A \exp(-\alpha t) \quad (4)$$

where

$$A = \frac{16 n_a n_g (n^2 + K^2)}{[(n_a + n)^2 + K^2][(n_g + n)^2 + K^2]} \quad (5)$$

and K is the extinction coefficient. A is found to be nearly equal to unity at the absorption edge.

The relation between α and incident photon energy $h\nu$ can be written as (Taue 1972, Szezyrbowski and Czapla 1977, Khawaja Ehsan and Tomlin 1975)

$$\alpha h\nu = C_1 (h\nu - E_g^d)^{1/2} \quad (6)$$

$$\alpha h\nu = C_2 (h\nu - E_g^i)^2 \quad (7)$$

for direct and indirect transition respectively, where C_1 and C_2 are two constants, $\alpha = 4\pi K/\lambda$ is the absorption coefficient, E_g^d and E_g^i are the direct and indirect band gaps respectively. The $(\alpha h\nu)^{1/2}$–$h\nu$ and $(\alpha h\nu)^2$–$h\nu$ plots for ZnTe undoped films of different thickness are shown in figure 3, and it is observed that both the direct and indirect band gaps decrease with the increase of thickness and hence particle size (which is calculated from x-ray line profile analysis). The direct band gap approaches its bulk value with the increase of thickness, but the values of indirect band gap are found to differ significantly from the bulk value (Thutupalli and Tomlin 1976, Mondal and Chowdhuri 1987). According to the band structure of ZnTe calculated by the nonlocal pseudopotential method (Chelikowsky and Cohen 1976) there is unlikely to be any indirect optical energy gap less than the direct band gap ($\Gamma_8 - \Gamma_6$). It is known that at lower photon energy transitions transition rules are relaxed (Lewis 1987) in the presence of a high density of defects, charge impurities and disorders at the grain boundaries (Redfield and Afromowitz 1967, Dow and Redfield 1970, 1972, Callaway 1964), so the activation energy obtained at lower energies may be due to an internal analogue of the Franz–Keldysh effect arising from electric field developed at the grain boundaries in the materials. Hence
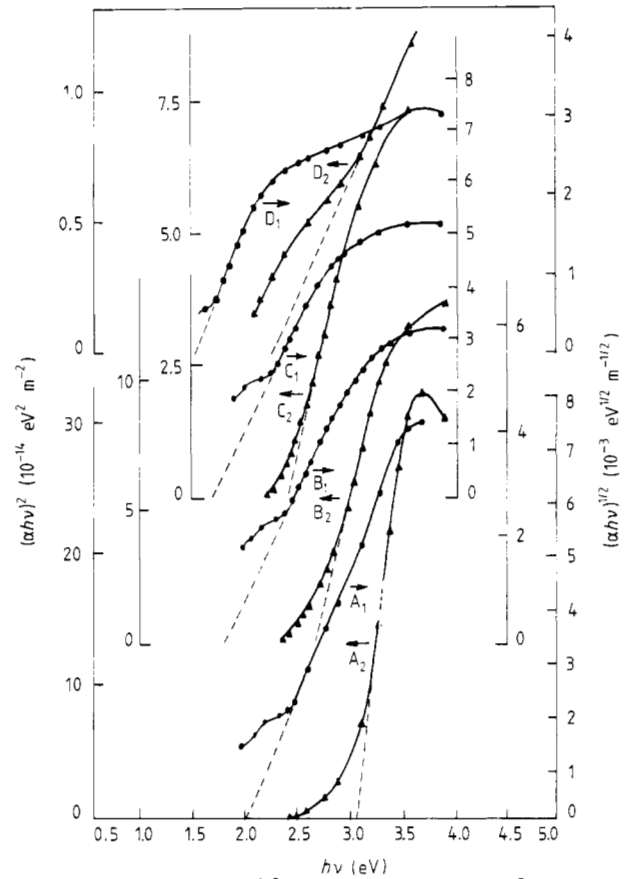

Figure 3. Plots of $(\alpha h\nu)^{1/2}$ against $h\nu$ and $(\alpha h\nu)^2$ against $h\nu$: A_1, A_2 for a 0.27 μm film; B_1, B_2 for a 0.42 μm film; C_1, C_2 for a 0.54 μm; D_1, D_2 for a 0.8 μm film. All deposited at room temperature (305 K).

this activation energy is due to a process which is different from the indirect transition. The measured direct band gaps (E_g^d) at lower thickness are found to be higher than that for the bulk value. However, such a variation of band gap with film thickness has not yet been reported in the literature. A comparison of E_g^d and E_g^i with thickness, particle size, microstrain and lattice constant for different films deposited at room temperature is shown in table 1. The decrease of E_g^d and E_g^i with increase of thickness is likely to be attributed to an increase of particle size, a decrease of RMS strain and an increase of lattice constant. The linear dependence between $(\alpha h\nu)^{1/2}$ and $h\nu$, and also between $(\alpha h\nu)^2$ and $h\nu$ in some films, has been observed to be distorted. A similar observation has been reported for CdTe films also (Vodakov *et al* 1960, Dubrovskii 1961, Nobel 1959).

The absorption of doped and undoped films deposited at 573 K substrate temperature was also measured, and the plots of $(\alpha h\nu)^{1/2}$ against $h\nu$ and $(\alpha h\nu)^2$ against $h\nu$ are shown in figure 4. The measured values of E_g^d and E_g^i are given in table 2. We observed that there was no appreciable change of E_g^d and E_g^i due to doping with $PbCl_2$ and BaF_2, whereas, for In doping both E_g^d and E_g^i decreased appreciably, which can be attributed to the segregation of impurities at the grain boundaries.
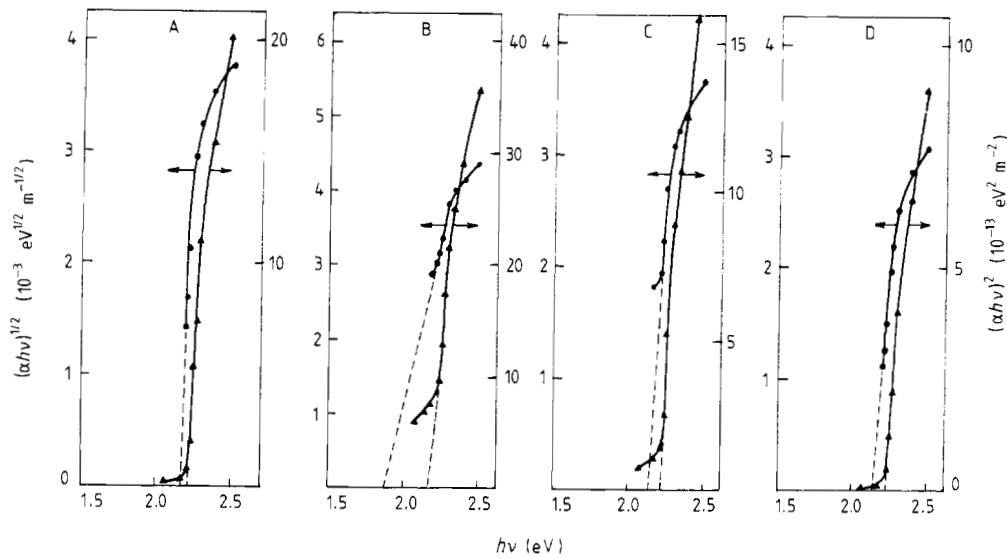
Figure 5 shows the variation of refractive index n

Figure 4. Plots of $(\alpha h\nu)^{1/2}$ against $h\nu$ and $(\alpha h\nu)^2$ against $h\nu$: A, ZnTe undoped, deposited at 573 K substrate temperature; B, ZnTe doped with In (6 wt%); C, ZnTe doped with PbCl$_2$ (6 wt%); D, ZnTe doped with BaF$_2$ (7 wt%).

Table 2.

Sample	Film thickness (μm)	E_g^d (eV)	E_g^i (eV)	n at $\lambda = 2.1\ \mu$m
ZnTe undoped	0.60	2.23	2.18	2.63
ZnTe doped with 6 wt% PbCl$_2$	0.63	2.21	2.15	2.54
ZnTe doped with 7 wt% BaF$_2$	0.66	2.23	2.13	2.54
ZnTe doped with 6 wt% In	0.62	2.18	1.88	2.45
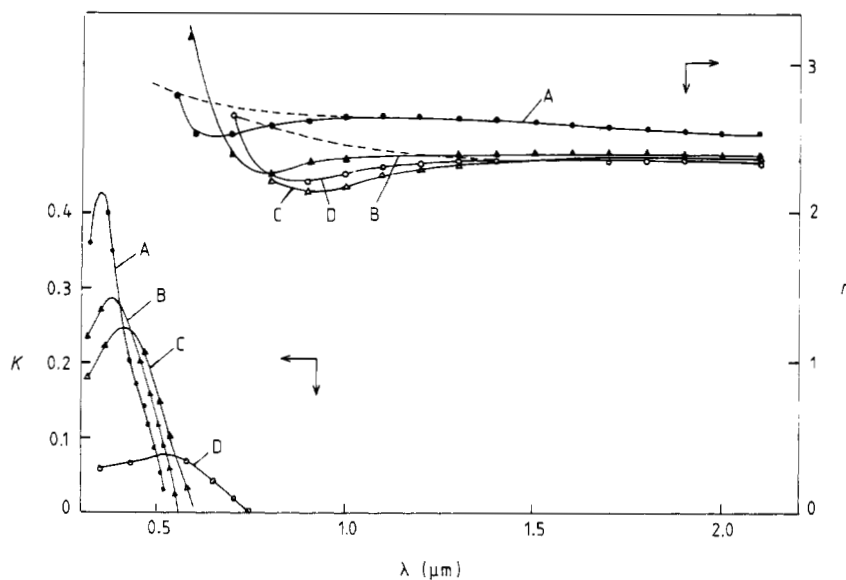
Figure 5. Plots of n against λ and K against λ for ZnTe (undoped) films of different thickness: A, 0.27 μm; B, 0.42 μm; C, 0.54 μm; D, 0.8 μm. The broken curves along with A and D are the theoretical plots using the experimental values of n calculated at higher values of λ.

and absorption constant K for undoped films of different thickness deposited at room temperature. It is interesting to note that the refractive index n of ZnTe films decreases monotonically with increasing thickness and this was found to be most noticeable near the absorption edge. This trend of variation is opposite to that of CdTe films reported by El Shazly and El Shair (1981), but n is independent of film thickness if the thickness is greater than 0.8 μm. An unexpected decrease of n was observed at shorter wavelengths. A
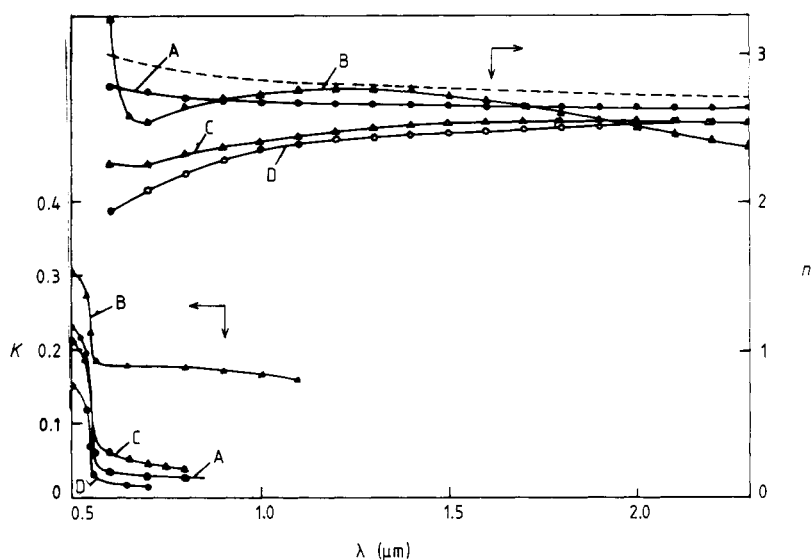
Figure 6. Plots of n against λ and K against λ for ZnTe doped and undoped films: A, ZnTe undoped, deposited at 573 K substrate temperature; B, ZnTe doped with In (6 wt%); C, ZnTe doped with PbCl$_2$ (6 wt%); D, ZnTe doped with BaF$_2$ (7 wt%). The broken curve shows the nature of variation of n with λ for bulk sample as given by Jensen and Torabi (1983).

similar observation has been reported by Manifacier (1976) for SnO$_2$ films. Such behaviour can be attributed to the strong effect of surface and volume imperfections on the microscopic scale (Pawlikowski 1985, Khawaja, Ehsan and Tomlin 1975, Bennett and Bennett 1967, Rouard and Messen 1977, Casset 1966, Berreman 1967, Bennet and Portens 1969, Beaglehole and Hunderi 1970, Thomas 1960). We also observed that such a deviation became more and more pronounced as the microstrain increased in the undoped films. The values of n for undoped films deposited at room temperature were found to be less than those of undoped films deposited at 573 K. Such a difference is mainly due to the larger grain size (150×10^{-4}) and lower strain (105×10^{-4}) in the films deposited at that temperature. The variation of n with λ for undoped films deposited at 573 K was found to be similar to that in bulk material (see figure 6). The decrease of n became significant for indium-doped films.

Filinski (1972) reported that the multiple scattering effects due to the scattering on microscopic inhomogenities may lead to a serious breakdown of the conventional Kramer–Kroning analysis of reflection and hence transmission spectra. However, in the case of thicker films, as they absorb strongly near and above their absorption edges, the effect of multiple scattering is less and the deviation of n is less. A theoretical plot of n against λ (figure 5) is shown for our thinnest ($0.27\,\mu$m) and thickest ($0.8\,\mu$m) films deposited at room temperature, using the experimental parameters and taking the index of refraction at the absorption edge $n(0) = 3.04$ (Jensen and Torabi 1983) in both cases at their corresponding absorption edges.

The variation of n and K for doped and undoped films deposited at 573 K substrate temperature is shown

in figure 6. It is seen that the effect of doping of In on the variation of n and K is appreciable, but the effect of PbCl$_2$ and BaF$_2$ is almost insignificant except at lower λ values where the effect of volume imperfections such as the impurities at grain boundaries is pronounced. The effect of In is found to be largest and most systematic for K.

4. Conclusions

(i) The values of E_g^d and E_g^i for ZnTe films are observed to vary with the thickness of the films when the films are deposited at room temperature. E_g^d approaches its bulk value with the increase of thickness of the film, but the estimated values of E_g^i are found to differ significantly from the reported values of the indirect band gap. Values of the direct band gap coincide exactly with the bulk value when the films are deposited at 573 K substrate temperature. Films deposited at this substrate temperature are found to be stoichiometric. The band gaps are modified with indium doping, but PbCl$_2$ and BaF$_2$ are observed to have no appreciable effect on the bandgap.

(ii) The values of optical constants (n and K) are found to be very sensitive to the thickness of the film deposited at room temperature if the thickness is less than $0.54\,\mu$m. A decrease of the values of n near the absorption edge has been explained by considering the effect of volume and surface imperfections. Such a deviation has also been observed in case of doped films. However, the nature of variation of n with wavelength is found to be similar to that of the bulk (figure 6) when the films are deposited at 573 K substrate temperature

without doping. A theoretical calculation has been made for the variation of n with wavelength near the absorption edge for the films deposited at room temperature.

Acknowledgments

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