Research on the property of deep ultraviolet transparent ZnO/β- Ga_2O_3 ZGO films in contrast to β- Ga_2O_3 films

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High-quality ZnO/ β - Ga_2O_3 (ZGO) films were fabricated on the sapphire substrates at the high vacuum atmosphere by laser molecular beam epitaxy (LMBE). The influence of substrate temperature in the ZGO film was researched. Moreover, β - Ga_2O_3 film was fabricated to compare to the ZGO films. It stated that the root mean square (RMS) of ZGO films has a tendency of becoming small with the substrate temperature increasing and X-ray diffraction peaks showed that the crystallization quality of ZGO films is best at 750 ℃ substrate temperature. With the increasing of the substrate temperature, the transmittance of ZGO films tended to high in the deep ultraviolet region.

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Keywords: ZGO film, Deep ultraviolet, Gallium oxide, Zinc oxide

1. Introduction

Gallium oxide (Ga_2O_3) is simconductive material with wide band gap which is high transparent in deep UV region. The enery band (E_g) is about 4.9 ev, which corresponde to the absorption boundray at about 250 nm [1-2]. Because of itself speciality, Ga_2O_3 has much preponderance for applications in various techonlogical areas, such as phosphors, gas sensors, transparent electronic device and ultraviolet photodetector [3]. Different growth technologies have been developed and used to grow Ga_2O_3 solid films, such as spray pyrolysis [4-5], sputtering [6], chemical vapor deposition [7] and pulser deposition [8]. Joo Han Kim used RF planar magnetron sputtering method to grow Mn – doped β - Ga_2O_3 single crystal whose luminescent properties has improved [10]. Kiyoshi reported that Si-doping can help to improve the photoluminescence of the β - Ga_2O_3 [11]. Cr-doped β - Ga_2O_3 were also fabricated by floating-zone method [12]. However, no detailed research on the effects of substrate temperatures of ZnO/ β - Ga_2O_3 (ZGO) films has been conducted so far. In this work, β-Ga_2O_3 and ZnO/β-Ga_2O_3 films have been prepared by laser molecular beam epitaxy in an oxygen environment without annealing. The effects of the substrate temperture on the structure and optical properties of the ZnO/β-Ga_2O_3 films were investigated using AFM, X-ray diffraction (XRD), Photoluminescence (PL), and Transmittance.

2. Experiment

ZGO films were fabricated on sapphire substrates by LMBE. An excimer laser (248 nm) was used as the laser source, which has a repetition rate of 1 Hz and pulse energy of 200 mJ. First, c-plane sapphire was used as a substrate and ultrasonically cleaned in acetone, alcohol and deionized water in turn. Second, after the vacuum chamber was pumped down to 10^{-5} Pa, the oxygen gas was introduced, until the pressure reached to 2×10^{-2} Pa. Third, the epitaxy process was carried out in a pure oxygen atmosphere with target-to-substrate distance of 50mm. Ga_2O_3 ceramic target (99.99 %) and ZnO ceramic target (99.999 %) were needed in sequence, the time of hetero-epitaxy was 3500 s and 1500 s in the process of fabrication respectively. The substrate temperature was setted to 650 ℃, 750 ℃ and 800 ℃ separately. In addition, Ga_2O_3 ceramic target (99.99 %) was needed only and other conditions are the same as the procedure above except that the substrate temperature was setted the point of 750 ℃. The Reflection high energy electron diffraction (RHEED) could synchronously monitor epitaxial layer and analyze fresh surface.

In this paper, Rigaku D/max-rB X-ray diffraction (XRD) spectroscopy with a Cu Kα line radiation source was utilized to examine the crystallinity of the thin films. What's more, thin films'surface and cross section morphology were observed by Atomic Force Microscope (AFM, PARK Autoprebecp) and Zeiss supra 55 field emission scanning electron microscope (FE-SEM). The transmission spectrum was detected by UV-visible spectrophotometer (U-4100), the photoluminescence and electrical properties were measured by Edinburgh Instruments FLS920 Steady-state fluorescence spectrometer (U.K.) with Xe lamp respectively. All of the above examinations were operated in room temperature.

3. Results and discussion

3.1 Surface morphology measurements

Cross section morphology of ZGO film at 800 ℃ by FE-SEM is observed in Fig. 1. Obviously, the part of high brightness is ZGO film whose thickness is about 100 nm. Besides, it is clearly that the thin film are uniform and compact. β - Ga_2O_3 single crystal belongs to the monoclinic system with space group C2/m, and the lattice parameters are a = 1.223 nm, b = 0.304 nm, c = 0.580 nm, β =103.83° [13]. When ZnO (002) grow epitaxially on β - Ga_2O_3 layer, the mixing of the rectangle in monoclinic crystal systems and hexagon in wurzite crystal systems results in lattice mismatching, Generally, the lattice mismatching effect the quality of crystalline film significantly but it couldn't influence the properties of the ZGO films.

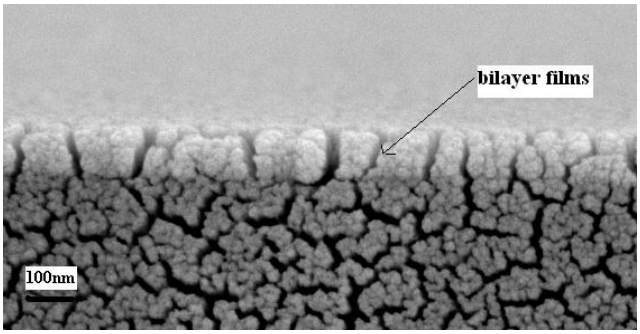

Fig. 1. Cross section morphology of ZGO films obtained at 800℃

AFM had been used to characterize the films. The surface morphology of ZGO films obtained at 650 ℃, 750 ℃ and 800 ℃ are observed in Fig. 2 (a) (b) (d), with 2 μm × 2 μm area, and Fig. 2 (c) shows β - Ga_2O_3 film which has been obtained at 750 ℃. Their root mean square (RMS) roughness is (a) 2.78 nm (b) 1.85 nm (c) 4.36 nm (d) 1.76 nm respectively. From the Fig. 2 (a), there are some granular structures on the surface of ZGO films, which should be an insular growth pattern due to atom migration energy shortage and consequently atom packing. We could deduce that the film morphology is composed of some vacancies, adding to poor crystallinity. Therefore, rough surface was formed. Fig. 2 (b) shows the sample has a smoother surface than the one obtained at 650 ℃ because of increasing of the atom migration energy with the substrate temperature increased. It can be seen that the Fig. 2 (c) sample has larger granular structures than the (a) sample and the (b) sample, distinct smooth surface was obtained by introducing a ZnO layer in the β - Ga_2O_3 film , moreover , the average grain size of films decreased by introducing a ZnO layer . The Fig. 2 (d) shows the sample obtained at 800 ℃ presents better smoothness than that of the film obtained at 750 ℃, but several nanopowder obviously emerge on the surface of ZGO films obtained at 800 ℃. That's because the Fig. 2 (a) (b) (d) were the ZnO films surface , and (c) is the Ga_2O_3 film surface, the (002) direction of ZnO was easy to grow , when the substrate temprature was 500℃, the ZnO film was crystallize well . With the rising of temperature, the root mean square (RMS) roughness slightly trend to smaller. There is a different of crystal structure between Al_2O_3 substrate and Ga_2O_3, so the surface of Ga_2O_3 film was not smooth, the root mean square (RMS) roughness was lagerer than the ZnO surface.

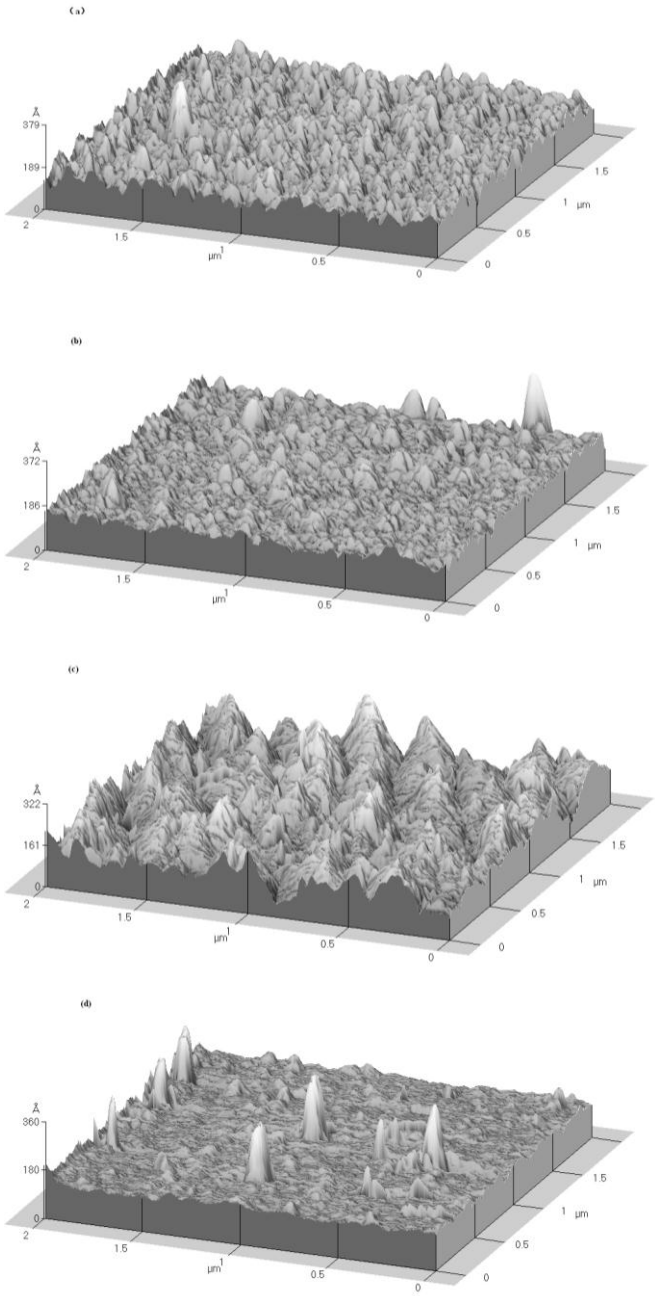

Fig. 2. Surface morphology of ZGO films with different temperature(a)650℃; (b)750℃; (c) β - Ga_2O_3 film obtained at 750℃; (d) 800℃

3.2 X-ray diffraction measurements

X-ray diffraction (XRD) pattern of ZGO films obtained at 650 ℃, 750 ℃ and 800 ℃ on sapphire substrate was shown in Fig. 3. The peak which is signed 'S' is attributed to the sapphire substrate (002). There is an evident diffraction peak at 34.22° (ZnO (002) peak), besides, two sharp peaks are found at 38.26° and 58.96°, from the PDF card (JCPDS 11-0370), the two peaks are β - Ga_2O_3 ($\bar{3}11$) and β - Ga_2O_3 ($\bar{6}03$) . In the sensitivity of the XRD instrument range, $ZnGa_2O_4$ and any zinc gallium oxides are not appearing in the interface between the ZnO layer and β - Ga_2O_3 layer. From the Fig. 3, it could be concluded that β - Ga_2O_3 layer grown at 650℃ has an amorphous structure but ZnO monocrystal is formed. β - Ga_2O_3 ($\bar{3}11$) peak and β - Ga_2O_3 ($\bar{6}03$) peak of β - Ga_2O_3 film grown at 750℃ are sharper than the ones of ZGO films grown at the same temperature. It is indicated that ZnO layer influence the crystallization of β - Ga_2O_3 layer perhaps because high temperature lasting goes against the crystallization of β - Ga_2O_3 layer. This has been proved else by the curve of ZGO films grown at 800℃. We surmise that at a suitable temperature, the atoms have enough diffusion activation energy to occupy the correct site in the crystal lattice and crystallization from the amorphous phase can be initiated [14].

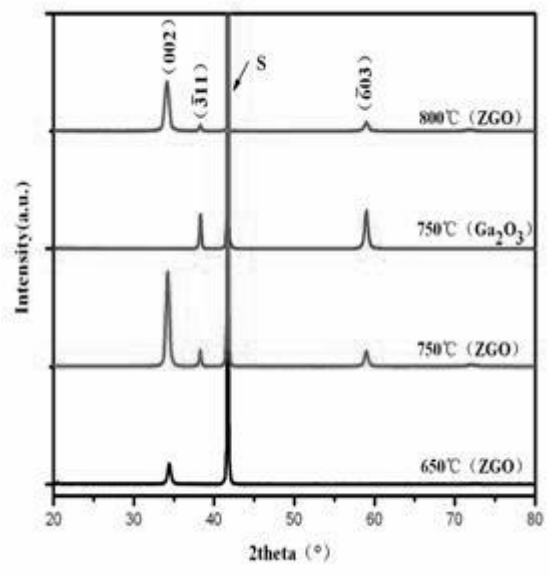

Fig. 3. XRD pattern of ZGO films on the sapphire substrate with different temperature. (a) 650℃; (b)750℃; (c) β - Ga_2O_3 film as-deposited at 750℃; (d)800℃

The Full Width at Half Maximum of ZGO films and β - Ga_2O_3 film is shown in Fig.4. According to Scherrer Equation

$$D = k\lambda / \beta \cos\theta \quad (1)$$

k is Scherrer constant, λ is X-ray wavelength, β is the FWHM, θ is the Bragg diffraction angle. We calculate that the particle size of the ZGO films which are grown at 750 ℃ is around 13.86~18.95 nm.

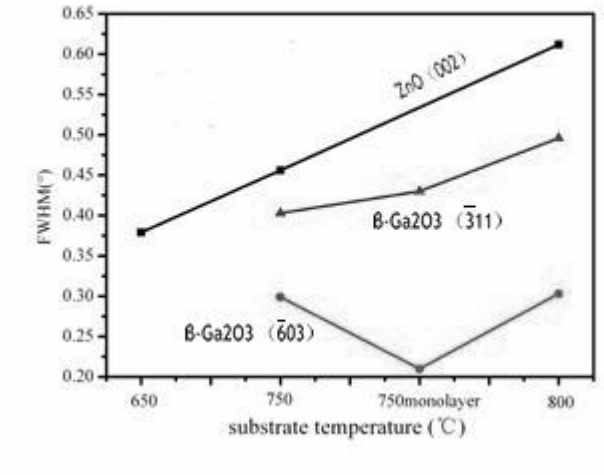

Fig. 4. The FWHM size and variation tendency of ZGO films and β - Ga_2O_3 film.

3.3 Optical properties

The transmittance spectrum of ZGO films and β - Ga_2O_3 film have been tested with UV-visible spectrophotometer, shown in Fig. 5 (a), and the sapphire substrate acted as a reference. ZGO films fabricated at different substrate temperatures in the range 650 ℃ to 800 ℃ exhibit a large average transmittance of over 95 % in the visible range and a novel characteristic of transparency in the deep ultraviolet region. However, β - Ga_2O_3 film presents a transmittance of about 77 % , it is lower than the transmittance of ZGO films in the visible range. The property of high transmittance is an important index to the transparent operating system (TOS) and one of the necessary conditions for display devices [15]. With the increasing of the substrate temperature from 650 ℃ to 800 ℃, the transmittance from 250 nm to 400 nm rises apparently. The absorption of ZnO was near 370nm, the absorbing was higher than transmission when the wave length under 370 nm, so the transmission rate was low, with the rise of temperature, the O in the ZnO will evaporation, the transmission increase, and close to the single Ga_2O_3 film. Fig. 4 (b) (c) shows the optical band gap calculated from the transmittance data using Tauc' Plot

$$(\alpha h\nu)^2 = C(h\nu - Eg) \quad (2)$$

where α is the optical absorption coefficient, the Eg is band gap energy, $h\nu$ is photo energy [16]. It is shown in Fig. 5 (b), in contrast to the optical band-gap of β -

Ga_2O_3 film, the optical band-gap of β - Ga_2O_3 layer of ZGO film with 800 ℃ is painted in the picture. The optical band-gap of Ga_2O_3 (4.6 eV) obtained from ZGO films is slightly smaller than that of β - Ga_2O_3 film (5.2 eV) and reported before (4.9 eV) [17]. This discrepancy may be associated with different tail states, crystallinity, and other factors [18]. Fig. 5 (c) shows the optical band-gap of the ZnO layer of ZGO films, with the substrate temperature being increased, the absorption edge blue-shifted is observed. This trend is in good agreement with the previous results of T. Rasada Rao et al [19]. From these results we may suggest that the substrate temperature influence significantly the optical band-gap of semiconductor materials.

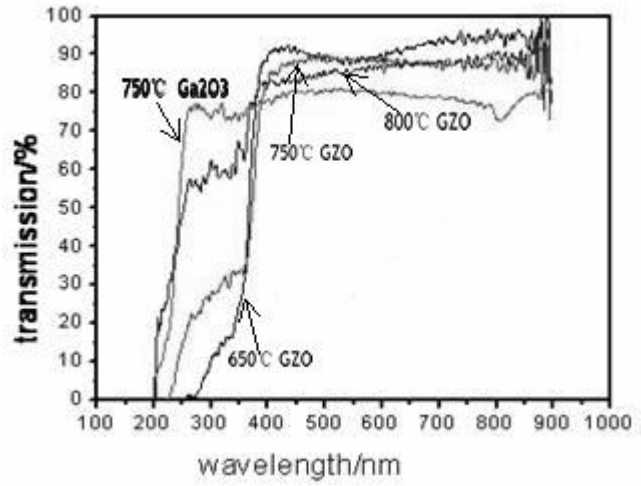

Fig. 5. (a) transmittance spectrum of ZGO films with different temperature and β - Ga_2O_3 film obtained at 750℃

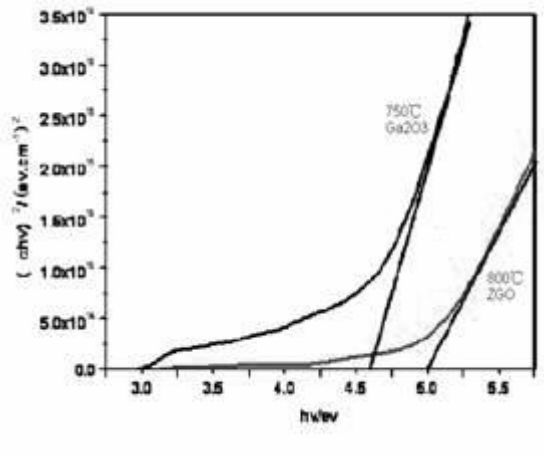

Fig. 5. (b) contrast between the bandgap of ZGO films depoisted at 800 ℃ and the one of the β - Ga_2O_3 film as-deposited at 750℃

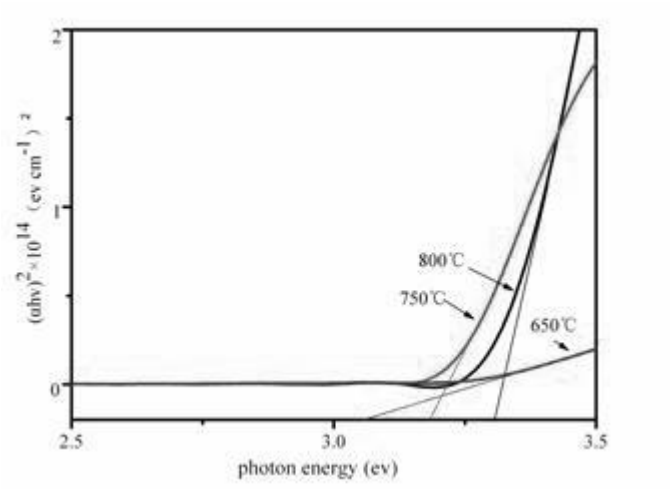

Fig. 5. (c) the optical band-gap of the ZnO layer as-deposited with different temperature.

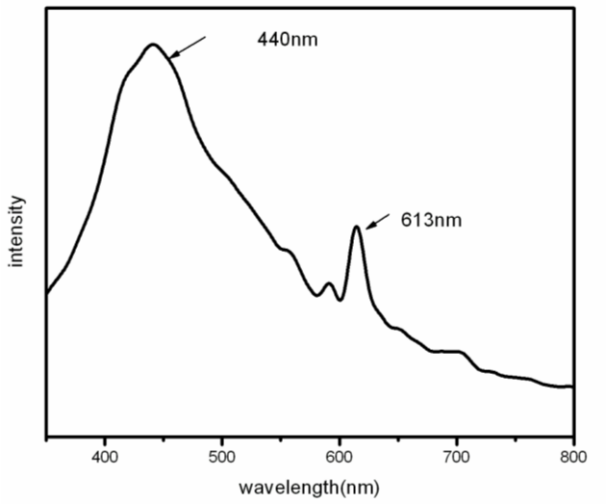

Fig. 6. The PL spectra of ZGO films obtained at 800℃

For future study of the optical properties of ZGO films, PL measurements were performed by FLS920 Steady-state fluorescence spectrometer with a Xe lamp as the excitation source (wavelength was 280 nm) at room temperature. As shown in Fig. 6 PL spectrum, two peaks were observed. The dominant emissions from as-deposited ZGO films located at a wavelength of around 440 nm (2.82 eV) and 613 nm (2.02 eV) , both of which were not caused by the bandgap absorption according to

$$Ev(ev) = \hbar\omega = 1240/\lambda \quad (3)$$

The peak at 440 nm corresponds to the blue-green spectral region. Blue-green luminescence of the films had been reported to be attributed to the formation of gallium vacancies [20], blue-green luminescence is close to the PL spectrum of zinc vacancies the films contained also, therefore, the peak at 440 nm was widen. Obviously, the red-orange luminescence at 613 nm appeared, the reason is

not clear, it may be a noise singal during the measurement.

4. Conclusion

We have investigated the structure and optical properties of ZGO films which had been fabricated by the LMBE method without annealing. The ZGO films have excellent surface and crystallinity between 750 ℃ and 800 ℃. In addition, the ZGO films have high transmittance in the deep ultraviolet region at 800 ℃. PL spectra of the as-deposited ZGO films reveal the dominant emission in the blue-green region. These ZGO films could be useful for the fundamental studies and many technological applications.

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References

[1] H. H Tippins Phys. Rev., **140**, A316 (1965).
[2] Z. Hajna, J. Miro, G. Kiss, F. Reti, P. Deak, R. C. Herndon, J. M. Kuperberg, J . Appl . Phys, **86**, 3792 (1999).
[3] M. Fleischer, W. Hanrieder, H. Meixner, Thin Solid Films **190**, 93 (1990).
[4] J. Hao, M. Cocivera, J Phys D:Appl Phys, **35**(5), 433 (2002).
[5] H. G. Kim, W. T. Kim, J Appl Phys,, **62**(5), 2000 (1987).
[6] M. Rebien, W. Henrion, M. Hong, etal. Appl. Phys. Lett., **81**(2), 250 (2002).
[7] K. H. Woo, K. N. Ho, Mater Sci Eng B,, **110**(1), 34 (2004).
[8] E. G. Villora, K. Shimamura, K. Kitamura, K. Aoki, Appl. Phys. Lett., **88**(3), 031105 (2006).
[9] Yijun Zhang, Jinliang Yan, Gang Zhao, Wanfeng Xie, Physica B **45**, 3899 (2010).
[10] Joo Han Kim, Kyung Ho Yoon J Mater Sci: Mater Electron, **20**, 879 (2009).
[11] Shimamura, Kiyoshi, Villora, Encarnacion G, Ujiie, Takekazu, Aoki, Kazuo Applied Physics Letters, **92**(20), 201914 (2008).
[12] Hirofumi Wakai, Yuuta Sinya, Akio Yamanaka Phys. Status Solidi C **8**(2), 537 (2011).
[13] Y. Tomm, P. Reiche, D. Klimm, T. Fukuda, J. Cryst. Growth **220**, 510 (2000).
[14] H. W. Kim, N. H. Kim, Mater. Sci. Eng., B. **110**, 34 (2004).
[15] J. B. Chen, L. Wang, X. Q. Su, L. Kong, G. Q. Liu, X. P. Zhang, Opt. Express. **18**, 1398 (2010).
[16] J. Tauc, R. Grigorovici, A. Vancu, Phys Status Solid. **15**, 627 (1966).
[17] M. Orita, H. Ohta, M. Hirano, H. Hosono, Appl. Phys. Lett. **77**, 4166 (2000).
[18] T. Oshima, T. Okuno, S. Fujita, Jpn. J. Appl. Phys. **46**, 7217 (2007).
[19] T. Prasada Rao, M. C. Santhosh Kumar, S. Anbumozhi Angayarkanni, M. Ashok, J. Alloys. Compd. **485**, 413 (2009).
[20] T. Harwig, G.. J. Wubs, G.. J. Dirksen, Solid State Commun. **18**, 1223 (1976).

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