RED-ORANGE PHOTOLUMINESCENCE IN TiO2: W

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Citation: Applied Physics Letters **16**, 341 (1970); doi: 10.1063/1.1653218
View online: http://dx.doi.org/10.1063/1.1653218
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/16/9?ver=pdfcov
Published by the AIP Publishing

the pulse rate. Two of the curves in Fig. 2(c) represent P_i and τ versus f as measured with an acousto-optically Q-switched system operating at the fundamental wavelength. The values for P_i and τ were inserted into Eq. (7) and the resulting function $P_{SH}(f)$ scaled to the experimental points shown in Fig. 2(c). The fit between experimental points and the theoretical curve is good considering the simplifications made in our model.

The results of this work indicate that although the theoretically available SHR power in the repetitively Q-switched mode is less than that for cw operation, a stable output, of higher average power, is obtained in the pulsed mode. This is due to the fact that for the higher peak powers in a Q-switched system the optimum SHR output occurs at a lower value of the nonlinear parameter. The low k_0 value permits the use of a mirror configuration which is well within the region of stable oscillation, yielding a fairly large beam waist. The configuration is thus relatively insensitive to slight misalignment and motion of the resonator elements. In the case of the cw system the optimum SHR output is obtained for a resonator operating in near-hemispherical configuration with an extremely small beam waist (and thus large k) which is sensitive to both transverse and axial motions of the resonator elements. In our cw system a compromise between stability and output optimization was made, which provided the system with an output coupling of less than optimum value and resulted in lower SHR power.

The authors wish to acknowledge the contribution of Miss Grace Graybowski in the experimental efforts described herein and Richard Sell for performing the computer calculations relating to optimization of the Q-switched SHG laser.

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RED-ORANGE PHOTOLUMINESCENCE IN TiO_2:W

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(Received 16 February 1970)

A red-orange photoluminescence emission band which peaks at approximately 2.02 eV was found in TiO_2:W. The excitation and emission spectra for this band are presented. The previously reported 1.46-eV photoluminescence emission band which was attributed to interstitial Ti^{3+} ions is found to be quenched in the presence of tungsten. This result is interpreted in terms of the reduction of interstitial Ti^{3+} ions in the presence of tungsten. The 2.02-eV band is tentatively identified as an electron transition from states at or just below the conduction-band edge to an acceptorlike level approximately 1 eV above the edge of the valence band.

In this letter, we wish to report the observation of a red-orange photoluminescence emission band in tungsten-doped TiO_2. In addition to this red-orange band which peaks at approximately 2.02 eV, the previously reported[1] doublet emission at 1.46 eV was also observed. This doublet emission has been tentatively identified[2] as electron transitions occuring within interstitial Ti^{3+} ions. Electron-spin-resonance measurements have identified[3] a spectrum, known as the "A" spectrum which is attributed to interstitial Ti^{3+} ions and is quenched in the presence of tungsten. The A spectrum is quenched because the formation of Ti^{3+} interstitials to compensate for intrinsic lattice defects or trivalent impurities will be inhibited in the presence of tungsten. The work described in this letter is an optical analog of that result, and furnishes additional evidence that the 1.46-eV emission band in TiO_2 arises from Ti^{3+} interstitials. Although the A spectrum as reported by Kingsbury *et al.* disappears above 8 °K, other EPR studies[4] have identified a spectrum attributed to Ti^{3+} interstitials at 78 °K in samples in which the interstitial Ti^{3+} were created by neutron and γ-ray irradiation. Since luminescence processes are not subject to the same restrictions as spin resonance processes, it is not surprising that the 1.46-eV band is readily detectable at 85 °K. It has also been found[5] that tungsten enters the rutile lattice substitutionally for Ti^{4+}. On this basis, it is expected that tungsten should behave electrically as a singly ionizable donor. Preliminary

electrical measurements indicate that this is the case. The dark conductivity of TiO_2:W is larger than the conductivity of comparable samples of undoped TiO_2. Also unlike undoped material, the temperature dependence of the dark conductivity of TiO_2:W exhibits a single activation energy of approximately 0.5 eV which dominates over more than five orders-of-magnitude variation of conductivity. These results indicate that the primary donor center in TiO_2:W is not Ti^{3+} interstitials or oxygen vacancies, but tungsten at Ti^{4+} sites.

The samples were TiO_2:W pellets of greater than 70% theoretical density. Samples ranging in tungsten concentration from 2×10^{-3} to 1×10^{-1} mole % were investigated. Typical emission spectra and excitation spectra for the two bands are shown in Fig. 1. The emission spectra were measured using a $\frac{1}{4}$-m scanning Jarrell-Ash monochromator (Model No. 82-410), and either an EMI 9558Q photomultiplier or a cooled RCA 7102 photomultiplier. The excitation spectra were measured by setting the Jarrell-Ash at the peaks of the emission spectra, and then scanning the incident xenon radiation using a Bausch and Lomb 500-mm grating monochromator and suitable filters. The luminescence emission spectra have not been corrected for the spectral response of the optical system.

The intensity of the 2.02-eV emission was fairly strong at 85 °K, but was rapidly quenched when the temperature was increased. The temperature dependence of the luminescence intensity for this band is different from that previously reported[1] for the 1.46-eV band. The broad and structureless 2.02-eV band was detected in all tungsten-doped samples studied. It did not appear in undoped samples. The intensity of the 2.02-eV band depended on the tungsten concentration as did the intensity of the 1.46-eV emission. As the tungsten concentration increased, the intensity of the 1.46-eV band decreased, indicating that the presence of tungsten suppresses the concentration of interstitial Ti^{3+} in agreement with the results of Kingsbury *et al.*[3] Because of the rapid thermal quenching of the 2.02-eV emission, only one weak low-temperature thermoluminescence glow peak was detected. The temperature of the maximum of this glow peak corresponded to the temperature of the maximum of the low-temperature glow peak of the 1.46-eV emission. Since the 1.46-eV emission is attributed[1] to an electron transition, and because of the thermoluminescence result, the 2.02-eV emission also must be attributed to an electron transition. From the figure, it is clear that the two excitation spectra are fundamentally different. The spectrum for the 1.46-eV emission is in agreement with previous results.[2] The spectrum for the 2.02-eV band extends well beyond the fundamental adsorption edge of TiO_2 into the visible region of the spectrum, indicating the presence of shallow acceptorlike levels. This result is consistent with the rapid thermal quenching of the 2.02-eV emission band.

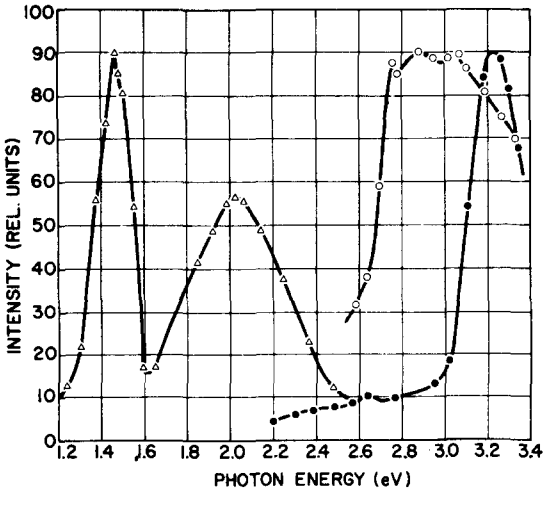

FIG. 1. Typical photoluminescence emission and excitation spectra for TiO_2:W at 85 °K. Δ–Emission using 7102 *PM*; ○–excitation spectrum of 2.02-eV band; and ●–excitation spectrum of 1.46-eV band.

Based on the excitation spectra, the ground state of this acceptorlike level, when unoccupied by a hole, is only a few tenths of an eV above the valence-band edge. It is proposed that the luminescence transition involved is from the excited state of this acceptor, which lies either in or just below the conduction-band edge, to the ground state of the acceptor when occupied by a hole. This model leads to a Frank-Condon shift between absorption and emission of approximately 1 eV. This acceptorlike level results from charge self-compensation. It is likely that doping with tungsten in addition to compensating trivalent impurities and reducing the concentration of interstitial Ti^{3+} also introduces intrinsic acceptorlike levels to maintain charge neutrality. Hence, the luminescence transition involved in the 2.02-eV emission is not directly due to the presence of tungsten, but arises from a center that is the result of charge compensation. In order to unambiguously determine the nature of the luminescence center involved, additional luminescence, as well as photoconductivity measurements, are in progress and will be the subject of a more complete paper.

The authors wish to thank Dr. Martin L. Harvill for the preparation of the samples and Paul Guay for valuable technical assistance.

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ELASTIC WAVE GENERATION BY A GUNN EFFECT OSCILLATOR COUPLED TO A PIEZOELECTRIC*

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(Received 2 March 1970; in final form 6 March 1970)

In a Gunn effect oscillator operating in the transit-time mode, domains of high electric field are formed periodically and travel through the device. When such an oscillator is placed close to the surface of a piezoelectric solid the moving high-field domains produce moving local stress concentrations in the piezoelectric, causing the radiation of elastic waves into the body of the piezoelectric and along its surface. The domain velocity is much higher than the elastic wave velocities, so the situation is similar to that of Cherenkov radiation, and the waves are emitted at a large angle to the direction of domain motion. Results are given on the generation of bulk and surface waves at a fundamental frequency of 114 MHz in a lithium niobate crystal coupled to a gallium arsenide Gunn effect oscillator.

It is well known that in several different types of semiconductor oscillator, domains of high electric field are formed and propagate at nearly constant velocity through the device.[1-3] If such an oscillator is adjacent to a piezoelectric solid, the electric fields associated with the moving domains cause the production of stresses and strains near the surface of the piezoelectric. These moving surface disturbances act as acoustic sources, resulting in the radiation of elastic waves into the body of the piezoelectric and along its surface.

In the work reported here, a Gunn effect oscillator operating in the transit-time mode, is placed close to a piezoelectric insulator. Since the Gunn domain velocity v_d is much larger than the elastic wave velocity v_a, this transducing action is similar to the production of acoustic Cherenkov radition,[4,5] and the acoustic radiation emerges at an angle $\theta_C = \cos^{-1}(v_a/v_d)$ with respect to the direction of domain motion. Substituting the typical velocities $v_d \approx 10^5$ m/sec and $v_a \approx 4.5\times10^3$ m/sec, we see that the acoustic Cherenkov angle is nearly $90°(\theta_C \approx 87.5°)$.

This type of elastic wave generation differs significantly from the previously reported[6,7] acoustic generation *within* Gunn effect oscillators; there generation due to the relatively weak piezoelectric coupling of the Gunn effect semiconductor material GaAs resulted in emission of low-amplitude elastic waves in a direction parallel to the direction of domain motion. In the present work the waves are radiated nearly normal to the direction of domain motion, and a strongly piezoelectric material may be used with the diode to yield the largest possible electromechanical coupling for the direction and mode of wave excitation desired.

The arrangement used to observe bulk wave generation is shown in Fig. 1. An n-GaAs Gunn effect diode which operates in the transit-time mode at 114 MHz is fastened with wax to the y-cut polished

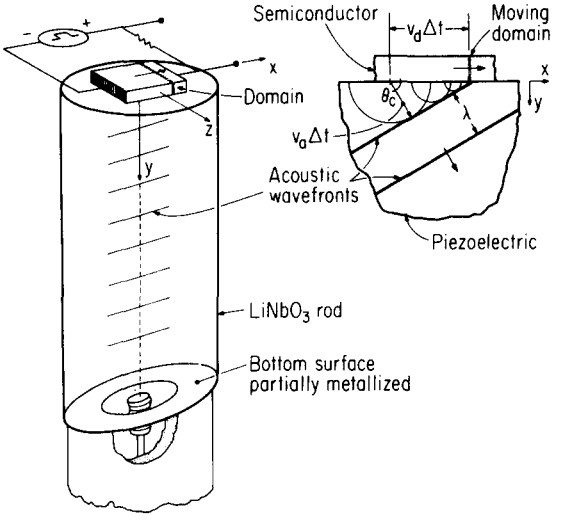

FIG. 1. Schematic sketch of Gunn effect oscillator on end of lithium niobate rod. Dimensions of diode in x, y, and z directions: 0.97, 0.23, and 0.52 mm, respectively. Rod length is 0.96 cm, diameter 0.5 cm. Current-monitoring resistor is 1 Ω. Inset shows each point in the interface acting as source of elastic waves. Wavelets add in phase to form acoustic wavefronts which propagate away at Cherenkov angle.