Photo- and Chemiluminescence from Wöhler Siloxenes

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ABSTRACT

The photo- and chemiluminescence of Wöhler siloxenes, $Si_6H_{3-x}(OH)_{3+x}$, in the two oxidation stages with $x = 0$: yellow siloxene and $x = 1$: red siloxene were studied. During slow oxidation both compounds exhibit a shift of the photoluminescence spectra at room temperature, but the position of the chemiluminescence is not affected. Our results support the buckled-layer structure of Wöhler siloxenes with the Si_6-ring in chair conformation as the building block. The Si-H bonds on the ring can be successively oxidized ($0 \le x \le 3$), leading to a shift in the photoluminescence spectrum. Total oxidation of all three Si-H bonds results in an unstable modification, which transforms rapidly to a new substance with distinctively different optical properties. The results on siloxene have common features with measurements on porous silicon. However, the quantitative differences in the spectra indicate that in porous silicon, the emission properties are not directly associated with Wöhler siloxenes.

Introduction

Silicon backbone materials[1] have attracted attention recently as an alternative way to explain the strong visible luminescence from porous silicon (PS).[2] In particular siloxene and its modifications were found to exhibit very similar optical properties compared to PS.[3]

We have recently identified the structure of siloxene, which was prepared according to the method first proposed by Wöhler.[4] The x-ray single-crystal analysis identifies the so-called Wöhler siloxene as 2D-poly[1,3,5-trihydroxocyclohexasilane].[5,6] Figure 1 gives a schematic view of the structure. A plane of Si_6 atoms, similar to the corrugated (111) plane in crystalline Si, is terminated by H or OH groups. The Si_6-ring in chair conformation with three Si-OH and three Si-H groups, all in axial position, is the basic building unit for this structure.

Efficient electroluminescence (EL) was reported from siloxene using liquid contacts.[7] To our knowledge, there is only one report on solid transparent contacts, which however gave only weak EL.[8] The EL from siloxene is not stable, due to chemical reactions in the material. On the other hand, chemical reactions can lead to a strong chemiluminescence (CHL), a common phenomenon, which often occurs during exothermic reactions. The energy released during the chemical reaction is transferred to a closeby radiative recombination center and generates the CHL. For siloxene CHL was reported already, however, in all cases oxidation was performed by immersing the samples in a liquid electrolyte. Under these conditions reactions can be quite fast and details of the changes in photoluminescence (PL) can be missed.

We report in this study on CHL and PL from siloxene, and we compare the results with published data on PS.

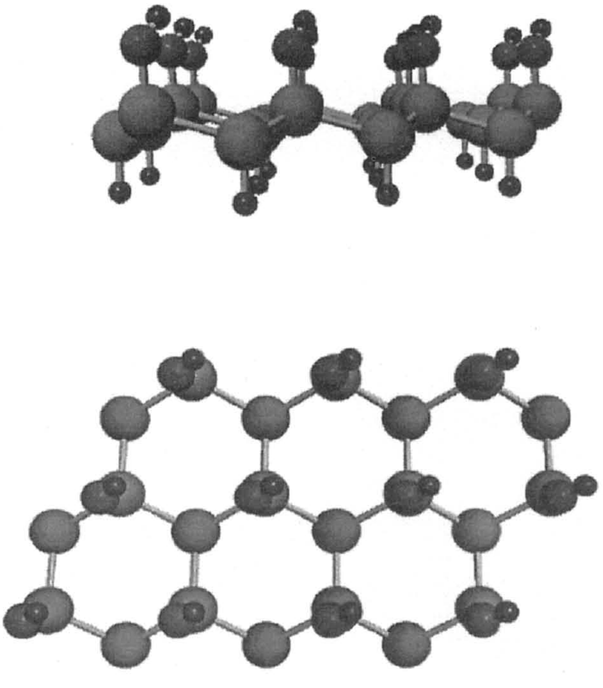

Fig. 1. Structural model of Wöhler siloxene [$Si_6H_{3-x}(OH)_{3+x}$, $x = 0$: yellow siloxene]. The Si planes are terminated by H and OH groups.

Experimental

Sample preparation.—Siloxene with yellow color (called yellow siloxene in the rest of the paper) was prepared according to Wöhler.[4] As all compounds of siloxene are sensitive to light, moisture, and oxygen, the reactions and handlings were performed under inert gas atmosphere (Schlenck technique and glove box with residual concentrations of O_2 and $H_2O \le 0.5$ ppm) and under the exclusion of daylight. About 100 mg of selected crystallites (with faces up to 1 mm^2 of commercial $CaSi_2$ (Aldrich) were immersed in 2 ml 37% HCl at 0°C in a dark tube using dry Ar as the inert gas. After a reaction time of 3 h the resulting bright yellow substance was filtered and washed 10 times with 2 ml H_2O (saturated with Ar) at 0°C to remove Ca and Cl ions and then dried at 110°C in vacuum for 1 h. A chemical analysis (Mikroanalytisches Labor Pascher, Remagen) yields a composition of Si [atom percent (a/o)] $64.8 \pm 0.5\%$, H (a/o) $2.37 \pm 0.05\%$, O (a/o) $20 \pm 1\%$. The ratio of Si:H:O was determined to be 6:5.6(1):3.0(1) (normalized to 6 Si atoms). This is very close to the ideal composition $(Si_6H_6O_3)_n$.

Siloxene with red color (red siloxene) was prepared in the following way. Again about 100 mg of selected crystallites of $CaSi_2$ were kept in a solution of 1 ml 37% HCl and 1 ml 5% aqueous H_2SO_3 under Ar at 0°C. Within a reaction time of 3 h the color of the siloxene flakes changed from yellow to dark red. Then the substance was filtered, washed ten times with ethanol (2 ml), twice with dimethoxyethane (1 ml), and dried in vacuum at room temperature. This material is extremely sensitive and deteriorates quickly under ambient conditions and light. After a few minutes the color changes from red to orange and back to yellow. This very quick deterioration makes it impossible to perform a chemical analysis on this compound.

Oxidation.—For the experiments ≈100 mg of siloxene was powdered and filled in quartz tubes (HSQ 300) under argon. The oxidation reaction was performed by slowly purging the tube with pure oxygen, using a controllable leak valve. The oxygen flow was ≈5000 sccm. Because of the very slow reaction the oxidation of the same sample took place over several days. After 5 days of oxidation under illumination yellow siloxene turns into a white sub-

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stance (in the following called white compound **1**). A chemical analysis of the white compound **1** yields a Si:H:O ratio of 6:5.9(1):6.2(1). Another oxidation reaction of yellow siloxene was performed by heating the substance in an opened Schlenck-tube in air at 200°C for 10 min. The chemical analysis of this white oxidation product (white compound **2**) gives a Si:H:O ratio of 6:4.2(1):9.0(1).

Optical measurements.—For the PL measurements of the yellow and red siloxene we used the 457.9 nm line of an argon-ion laser for excitation. The white oxidation products (compound **1** and **2**) have emissions in the blue range and were excited by the UV lines of an argon laser (363 nm). The excitation power was 4 mW/cm^2. For the CHL measurements the laser was turned off, and the oxygen gas was slowly introduced into the tube through a capillary. The emission spectra were detected by a cooled GaAs-photomultiplier with a cutoff wavelength at 900 nm. All measurements were performed at ambient temperature and pressure.

The measurements of the infrared transmission of the samples was performed in a Bruker IFS 66 spectrometer. The material had to be pressed into KBr-pellets under inert gas.

Results

Yellow siloxene.—Yellow siloxene gives rise to an intense room temperature PL in the green range of the visible spectrum as shown in curve (b) of Fig. 2. The PL has a maximum at 2.3 eV and a spectral width of 330 meV (full width at half maximum = FWHM). The PL spectra after short [30 min: Fig. 2(c)] and long [1 day: Fig. 2(d)] oxidation times are presented, too. All spectra are normalized to their maximum intensity and shifted in intensity scale for better clarity. The relative intensities of the different spectra can be derived by dividing the spectra in Fig. 2 by the given factors. Oxidation for 1 day reduces the PL intensity by a factor of $\approx$3 as compared to the intensity of the as-prepared sample. The PL spectra exhibit a clear shift to smaller energies E_{max} = 2.15 eV at the beginning of oxidation, there is also a remarkable broadening of the band up to 590 meV [curve (c)]. Further oxidation (starting at $\approx$1 h) leads to a spectral shift back to green (2.33 eV after 1 day).

The degradation of the PL intensity with oxidation time is strongly enhanced by illuminating the sample during the oxidation process with the laser. Under these conditions the total PL intensity decreases with a time constant (1/*e* time) of about 30 min, compared to about 1 day, when the oxidation was performed in the dark. The oxidation under illumination for 5 days shifts the PL more toward blue with a maximum at about 2.45 eV, see Fig. 2(e) and is about 160 meV broader than the one which oxidized for 1 day without illumination [see Fig. 2(d)]. The inhomogenous oxidation generates several PL centers in this sample, which all contribute to the broad spectral width of the PL.

The CHL of yellow siloxene after turning on the oxygen flow is shown in Fig. 2(a). The maximum of this emission is centered at 2.17 eV and the width of the band is $\approx$400 meV (FWHM). Whereas the maximum of the PL shifts with oxidation, the CHL remains at the same energy position and exhibits no pronounced increase in width. The CHL intensity depends on the rate of the chemical reaction, and the efficiency of transferring the excitation to luminescing states. The CHL intensity is in our experiments very low and not visible to the eye in the dark. However, measurements performed by detecting the whole sample emission without spectral resolution have shown that the total luminescence intensity is about 24.000 photons/s × cm^2, which is not far from the limit for light perception (30.000 photons/s × cm^2).[9] At a constant oxygen flow no noticable change of the CHL intensity was observed even after some hours and only after some days the CHL disappeared. This behavior indicates a very slow chemical reaction.

The reduction of PL intensities of the siloxene samples and the shift of the PL emission is also correlated with a change in the color of the powder, which turns to yellowish white after storage in oxygen atmosphere. After long illumination times the signal reduces further and the irradiated areas become white. The PL emission of the substance shifts under these conditions toward the blue. Such a relationship between the change of substance color during oxidation with strong oxidizing acids and luminecsence colors was already described many years ago by Kautsky *et al.*[10] It is known from Ref. 11 that siloxene undergoes structural transformations during heat-treatment, resulting in the loss of the long-range order. In our case, light in the presence of oxygen causes a transformation of the Si$_6$H$_3$(OH)$_3$ planar structure by breaking Si-Si-bonds and incorporating more oxygen. This behavior is supported by the results of the chemical analysis of the white samples (white compound **1**), which contain a higher oxygen concentration [Si:H:O = 6:5.9(1):6.2(1)]. The composition indicates an intermediate step of the oxidation of siloxene. The white compound **2** produced by heat-treatment of yellow siloxene under oxygen has a composition of Si:H:O = 6.0:4.2:9.0. This substoichiometric hydroxide resembles very much the HSiO$_{1.5}$ reported by Kautsky,[12] where all Si-Si bonds of siloxene are oxidized into Si-O-Si. The last step of this process would be the creation of SiO$_2$.

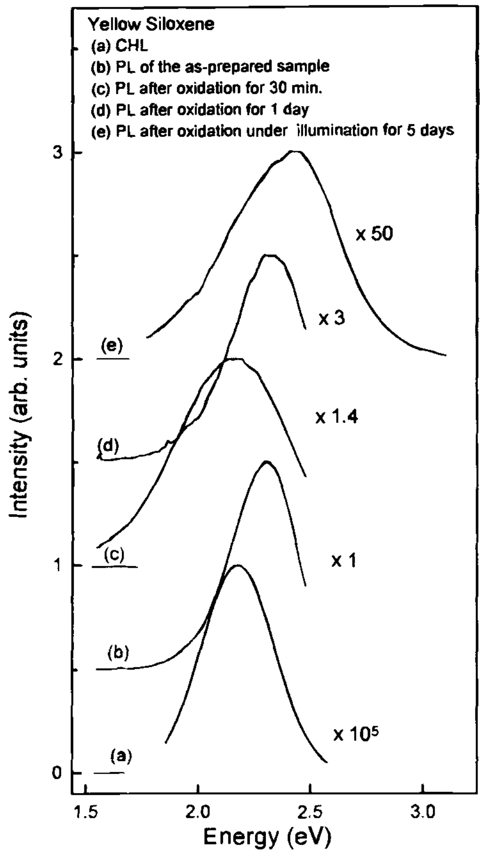

Fig. 2. Emission spectra of yellow siloxene (a) CHL, (b) PL of the as-prepared sample before oxidation, (c) PL after 30 min oxidation in oxygen gas, (d) PL after 1 d oxidation in oxygen gas and (e) PL after 5 d oxidation in oxygen gas under illumination.

The degradation of the PL after long oxidation times at higher temperatures is related to the increased density of dangling bonds in this material.[13] A similar process was suggested by Tischler *et al.*[14] to explain the decrease in PL of PS in the presence of oxygen and light.

Red siloxene.—The PL emission of red siloxene (maximum at 2.17 eV, FWHM = 390 meV) before the slow oxidation in oxygen gas, curve (b) of Fig. 3, is red shifted compared to the PL of yellow siloxene. Red siloxene is very reactive, resulting in a rapid disappearence of the red part of the PL spectrum during oxidation. The PL spectrum measured after an oxidation time of $\approx$30 min is already strongly green shifted and has a maximum at 2.28 eV [see Fig. 3(c)], very similar to the one of yellow siloxene. The degradation of the PL intensity is also comparable to that found for yellow siloxene.

The CHL spectrum of red siloxene shown in Fig. 3(a) is red shifted compared to the PL, but exhibits a much sharper linewidth (FWHM = 290 meV) compared to the CHL of yellow siloxene (FWHM ≈ 400 meV). Again the spectral distribution and the position of the maximum of the CHL do not change even after many hours of oxidation.

Discussion

There is a distinct difference between the PL and CHL spectra, which originates from the different excitation processes. The laser excites all possible recombination centers with different emission energies in the siloxene structure. A change in the peak position of the PL is then due to a change in the concentration of the different recombination centers. The CHL is, however, specific to the structure of the recombination center. The chemical reaction excites only one type of recombination centers with one emission energy.

The PL spectrum of Wöhler siloxene shifts with oxidation time. A similar behavior was found already in Kautsky siloxene.[10] Kautsky siloxene consists of a structure similar to Wöhler siloxene, however, the sixfold Si rings are now interconnected by oxygen atoms, leading to a Si_6 ring structure with all Si atoms of the ring containing one Si-H bond. In a number of experiments Kautsky and others supported an intuitive model, where by stepwise substitution of the six H atoms by OH groups the color of the substance and the PL was red shifted.[10,15]

Our measurements determine for the Wöhler compounds a similar shift in the color of the samples and the PL, and we correlate this behavior also to the number and extent of substitution of the hydrogen atoms by OH substituents. However, contrary to Kautsky siloxene, in Wöhler siloxene only three Si-H bonds exist on the Si ring and only three oxidation steps are possible. The change in PL emission of siloxene in our case from green before oxidation into yellow-orange during oxidation is then ascribed to the oxidation of one H atom into an OH. The energy released by this oxidation excites the luminescence from the Si_6 ring. Therefore, the position of CHL from yellow siloxene $[Si_6H_{3-x}(OH)_{3+x}$ with $x = 0]$ corresponds to the first oxidation step, which is the red siloxene ($x = 1$), prepared by wet chemical oxidation. In Fig. 4 the position and the shape of the PL from red siloxene are identical to those of the CHL of yellow siloxene.

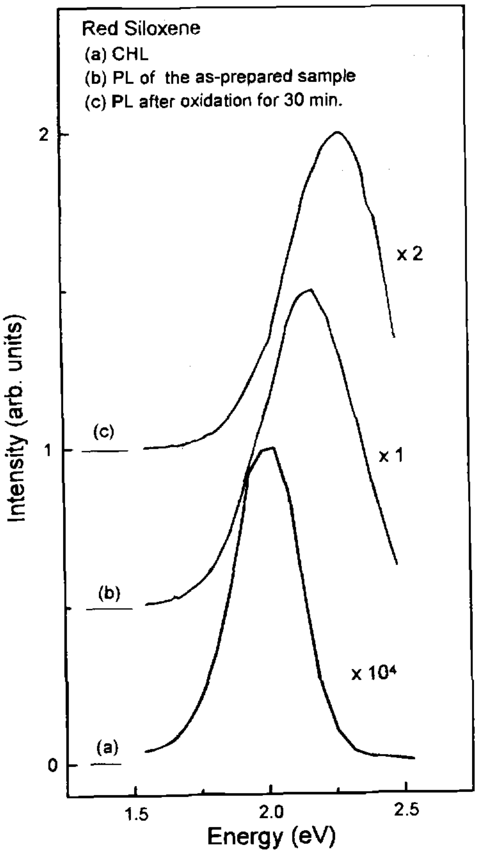

Fig. 3. Emission spectra of red siloxene (a) CHL, (b) PL of the as-prepared sample before oxidation, (c) PL after 3 min oxidation in oxygen gas.

The second oxidation step, the substitution of the second H atom by OH, can be observed in the CHL of red siloxene. The maximum of the spectrum is shifted by about 140 meV compared to the PL of this compound. The energy transfer to the ring seems to be very selective, only the oxidation of the second H atom gives rise to CHL. Oxidation of the third atom occurs, as evidenced by the extremely broad PL spectrum of yellow siloxene after short oxidation with a part of the emission in the red. The CHL of this oxidation process is presumably far too weak and not detectable in our experiment.

After oxidation of all Si-H groups on the ring, the structure changes drastically. The planar structure of siloxene is destroyed and a substoichiometric oxide is formed. The structural changes are clearly revealed in the infrared (IR) transmission spectra. In Fig. 5 the IR spectra of the yellow siloxene and the white compound **1** and **2** are shown. The characteristic vibrational modes of the planar siloxene structure are the Si-Si stretching vibration of the Si-plane at 518 cm^{-1}, the Si-H stretching mode at 2100 cm^{-1}, and the broad O-H stretching mode at around 3400 to 3600 cm^{-1}.[16] In Fig. 5(a) all three modes are present. In addition, vibrational modes due to the imperfect structure of our siloxene samples show up, *e.g.*, the Si-O-Si stretching at 1050 cm^{-1} of oxygen atoms in the plane. Additional weak lines at 2300 and 2900 cm^{-1} are due to CO_2 absorption contained in the air and HCl vibrational modes originating from the preparation of the samples.[17] In the oxidized samples [Fig. 5(b) and (c)] changes in the O and H related modes appear. The Si-H mode at 2100 cm^{-1} is reduced, but the mode of the oxygen atoms in the plane at 1050 cm^{-1} increases. There is also an increase and broadening of the O-H stretching mode, presumably due to the presence of water. Pronounced changes with oxidation occur also around 800 cm^{-1}, however, the assignment of these modes to different Si-OH stretching modes or Si-H bending modes is not clear at the moment.

Unfortunately, it was not possible to measure the IR spectra of red siloxene. The preparation of the IR samples by pressing them in KBr pellets requires some experimental steps leading to further oxidation of the samples. The observable IR spectra of red siloxene were, therefore, very

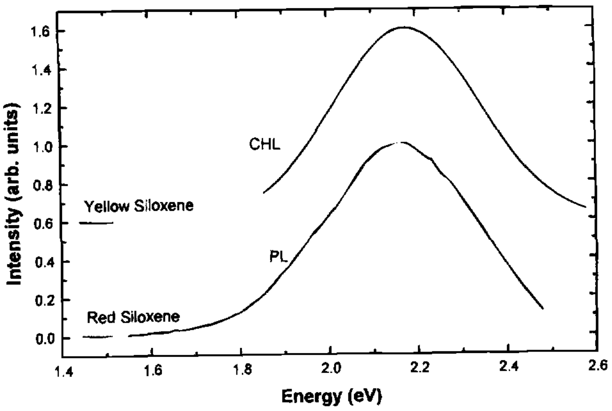

Fig. 4. Comparison between the CHL spectra of yellow siloxene and the PL spectrum of red siloxene prepared by wet oxidation of yellow siloxene.

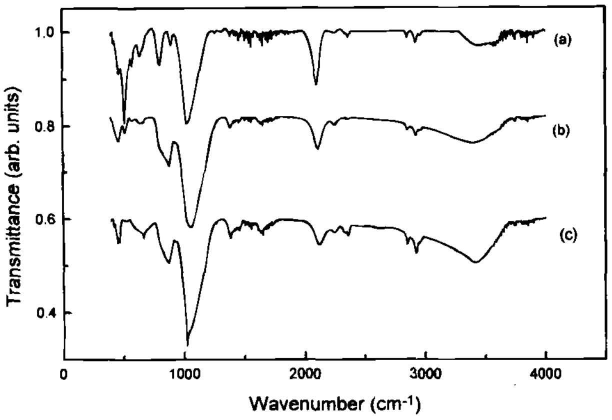

Fig. 5. Infrared transmittance of yellow siloxene (a) as-prepared, (b) after oxidation under illumination for 5 days, and (c) after 200°C annealing in air for 10 min. Spectra are shifted in transmittance for better clarity.

similar to those of samples which were oxidized under illumination [Fig. 5(b)]. These samples, which are white and exhibit a PL in the blue, are clearly inhomogenous. There is still evidence for a planar structure from the remaining absorption at 520 cm^{-1}. The Si-H mode (2100 cm^{-1}) is reduced, but there is an increase in the OH mode (3500 cm^{-1}) indicating the replacement of the H bonds by OH bonds. Incorporation of additional O in the Si plane leads also to an increase and shift of the Si-O-Si mode. The additional Si-O-Si bonds are also responsible for the weak absorption at 2250 cm^{-1}, which corresponds to the Si-H vibration with Si backbonded to three oxygen atoms.

After heat-treatment at 200°C in air (white compound **2**) the PL has a maximum at 2.6 eV (spectrum is not shown here). We find no evidence for Si planes anymore. The IR spectrum Fig. 5(c) shows only minor changes compared to Fig. 5(b). There is a decrease in the Si-H modes (2100 cm^{-1}) but still an increase in the O-H modes (3500 cm^{-1}).

The infrared spectra prove that the siloxene planar structure is destroyed by oxidation. Oxygen is incorporated in the planes, leading to a destruction of the regular structure. Characteristic vibrational modes associated with the structure of the first oxidation steps are not detectable by IR absorption, due to the oxidation during sample preparation. The structures can only be monitored by the shift of the PL and CHL toward lower energies.

There are many similarities between the CHL of siloxene discussed here and the CHL of PS reported from other groups. For example, McCord *et al.*[18] observed a white residual which remains on the surface of PS after the flash of CHL at the end of oxidation. This corresponds to our observations of the color change of siloxene from yellow before oxidation to white at the end of the CHL emission. Another common feature is that in both materials, PS and siloxene, the CHL emission always occurs at longer wavelengths than the PL emission. Furthermore, the CHL and PL in both cases are sensitive to ambient conditions.[19,20] Although, there are many qualitative similarities between the PL and CHL of PS and Wöhler siloxenes, there is no quantitative agreement in the spectral position and linewidth of the emission processes in the two materials.

Conclusions

The chemiluminescence of yellow and red Wöhler siloxenes under the influence of oxygen appears at energies smaller than the photoluminescence emission of the substances. The CHL is generated by oxidation of the Si-H bonds of the planar structure. Three primarily different oxidation steps are possible in yellow siloxene. The first two of them are monitored by CHL. The degradation of the PL intensity caused by light and oxygen is due to an irreversible transformation of the substance into a substoichiometric oxide. Our results presented here have common features with CHL measurements on PS, however, the quantitative differences in the spectral positions indicate that in PS the emission properties are not directly associated with Wöhler siloxenes.

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REFERENCES

1. Y. Kanemitsu, *Phys. Rep.*, **263**, 1 (1996).
2. L. T. Canham, *Appl. Phys. Lett.*, **57**, 1045 (1990).
3. M. S. Brandt, H. D. Fuchs, M. Stutzmann, J. Weber, and M. Cardona, *Solid State Commun.*, **81**, 307 (1992).
4. F. Wöhler, *Liebigs Ann. Chem.*, **127**, 257 (1863).
5. U. Dettlaff-Weglikowska, S. Finkbeiner, W. Hönle, A. Molassioti-Dohms, and J. Weber, To be published.
6. W. Hönle, U. Dettlaff-Weglikowska, S. Finkbeiner, A. Molassioti-Dohms, and J. Weber, Paper presented at the Symposium on *Tailor-Made Silicon-Oxygen Compounds - From Molecules to Materials*, Sept. 3-5, 1995, CIR, Bielefeld, Germany, To be published.
7. E. A. Meulenkamp, P. M. M. C. Bressers, and J. J. Kelly, *Appl. Surf. Sci.*, **64**, 283 (1993).
8. M. Stutzmann, *Phys. Status Solidus* (B), **192**, 273 (1995).
9. A. K. Campbell, *Chemiluminescence*, Horwood, Southampton, England (1988).
10. H. Kautsky and H. Zocher, *Z. Phys.*, **9**, 267 (1922).
11. H. Ubara, T. Imura, A. Hiraki, I. Hirabayashi, and K. Morigaki, *J. Non-Cryst. Solids*, **59 & 60**, 641 (1983).
12. H. Kautsky, *Z. Naturforsch.*, **7b**, 174 (1952).
13. M. S. Brandt, M. Rosenbauer, and M. Stutzmann, *Mater Res. Soc. Proc. Vol.* **298**, 301 (1993).
14. M. A. Tischler, R. T. Collins, J. H. Stathis, and J. C. Tsang, *Appl. Phys. Lett.*, **60**, 639 (1992).
15. H. Kautsky and G. Herzberg, *Z. Anorg. Ch.*, **139**, 135 (1924).
16. H. D. Fuchs, M. Stutzmann, M. S. Brandt, M. Rosenbauer, J. Weber, A. Breitschwerdt, P. Deák, and M. Cardona, *Phys. Rev.*, **B48**, 8172 (1993).
17. *Tables of Wavenumbers for the Calibration of Infrared Spectrometers*. International Union of Pure and Applied Chemistry, Commission on Molecular Structure and Spectroscopy PC1, LA2, Butterworths, London (1961).
18. P. McCord, S.-L. Yau, and A. J. Bard, *Science*, **257**, 68 (1992).
19. E. A. Meulenkamp, T. J. Cleij, and J. J. Kelly, *This Journal*, **141**, 1157 (1994).
20. P. C. Searson, S. M. Prokes, and O. J. Glembocki, *ibid.*, **140**, 3327 (1993).