APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 5, 295–301 (1991)

Thin films of peroxopolytungstic acids: applications to optical waveguide components

Kiminori Itoh, Tohru Okamoto, Shuhei Wakita, Hiroshi Niikura and Masayuki Murabayashi
Institute of Environmental Science and Technology, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240, Japan

Thin films of peroxohetero(carbon)polytungstic acid (CW-HPA) and carbon-free isopolytungstic acid (W-IPA) were prepared, and examined in terms of optical and etching properties. Thermal decomposition was found to give good results in removing excess hydrogen peroxide (H_2O_2) during the preparation of CW-HPA and W-IPA. It was shown for the first time that thin films of CW-HPA and W-IPA have very high refractive indices (larger than 2.0) when sufficiently dried. Optical waveguide (OWG) characteristics of these films were examined using a slab-type OWG structure and ARROW (Antiresonance Reflection Optical Waveguide)-type structures. An embossing technique was applied to make diffractional grating couplers.

Keywords: Peroxopolytungstic acid, etching, refractive index, optical waveguide, diffractional grating, photochromism

INTRODUCTION

Spin-coatable, amorphous, inorganic compounds are interesting as optical materials such as antireflection coatings and thin film optical waveguides (OWGs). For instance, spin-coatable amorphous iron(III) phosphate ($FePO_4$) film OWGs were reported recently;[1] however, they show relatively large attenuation of guided light (*ca* 50 dB cm^{-1}).[2,3] Also, mixtures of titanium dioxide (TiO_2) and silica (SiO_2) are amorphous, and were reported to be good OWG materials, but they require curing at rather high temperatures (500 °C).[4] Peroxopolytungstic acids are attractive in this respect; that is, they can be made into hard thin films with spin-coating and at low drying temperatures, below 100 °C. In fact, it has been proved that they are good spin-coatable inorganic resists.[5]

Thus, in this report, we examine optical and chemical properties of peroxohetero(carbon)-polytungstic acid (CW-HPA)[6] and carbon-free isopolytungstic acid (W-IPA),[5,6] mainly aiming to apply these compounds to optical waveguide (OWG) components such as thin-film OWGs and grating couplers. In addition, a facile method of preparing CW-HPA and W-IPA is described.

EXPERIMENTAL

Preparation of CW-HPA and W-IPA

Tungsten carbide (WC) or tungsten powder (3 g each) was first dissolved in H_2O_2 (15 cm^3 of 30 % solution, or 30 cm^3 of 15 % solution) in a 300 cm^3 beaker; the former powder is for CW-HPA, and the latter for W-IPA.[6] Tungstic acid (H_2WO_4) can also be used for W-IPA.[7] It is necessary to remove excess H_2O_2, which causes precipitation.[6] H_2O_2 is, however, indispensable in the structure of CW-HPA and W-IPA; empirical chemical formulae are $CO_2{\cdot}12WO_3{\cdot}7H_2O_2{\cdot}nH_2O$ for CW-HPA and $12WO_3{\cdot}7H_2O_2{\cdot}nH_2O$ for W-IPA, where n is *ca* 25.[6] A platinum gauze with platinum-black catalyst used in the original paper decomposes H_2O_2 very quickly, but sometimes leads to formation of precipitate because of excess decomposition of H_2O_2. It was found that thermal decomposition of H_2O_2 is effective for this purpose.[3]

The colorless solution, with small amounts of bubble (O_2) formation, obtained after the dissolution reaction was transferred to a 20–50 cm^3 test-tube, and was placed in a thermostated bath at 60 °C; the solution immediately formed bubbles vigorously. The color of the solution became pale yellow after 60 min and deep yellow after *ca* 100 min. The solution continuously formed bubbles during the heating process. A white precipitate appeared when the heating was carried out

0268-2605/91/040295-07$05.00

Received 27 February 1991
Revised 24 April 1991

until bubble formation stopped. In addition, a container with a large opening, such as a beaker, gave precipitate when used for heating the reacted solution, probably because O_2 release was too quick. The solution was transferred to a shallow dish, after heating for 70–100 min and was dried at room temperature with blowing air. Yellow glassy CW-HPA and W-IPA were thus obtained.

We describe the detail of the preparation of CW-HPA and W-IPA above, because it is rather difficult to follow the original method employing the platinum catalyst. We believe that the thermal decomposition of H_2O_2 shown here is easier to control.

Preparation of thin films of CW-HPA and W-IPA, and their chemical and optical properties

A 0.45 g portion of the glassy CW-HPA or W-IPA was dissolved in 1 cm^3 of water, and coated onto a glass slide or an acrylic resin plate with a spin-coater. Particulate impurities in the solutions were removed with a membrane filter (pore size 0.2 μm) before coating. The films were hardened by drying at 80–120 °C or by UV irradiation (low-pressure mercury lamp, 10 W).

The thicknesses and complex refractive indices of these films were estimated using a MOSS Model ES4-OMA ellipsometer (SOPRA, by courtesy of Seika Corporation) at wavelengths of 250–850 nm, and with a Model El-101 (NIIC) at 633 nm. The films of CW-HPA and W-IPA were etched with various etchants, i.e. water, hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and potassium hydroxide (KOH) at different concentrations, and the etching velocity was estimated.

Optical waveguides (OWGs)

The OWG characteristics of the films were measured with the set-up shown in Fig. 1. The coupler prism is made of SF-14 glass ($n = 1.75$), and the turntable is step-motor-driven. A photohardening resin ($n = ca$ 1.5) was used to make ARROW (Antiresonance Reflection Optical Waveguide)-type OWGs (cf. Fig. 8). Potassium ion (K^+)-doped glass slides[8] were used as OWGs with a thick light-guiding layer when necessary. A commercial diffraction grating (1200 lines mm^{-1}) was used as a master grating in an embossing technique to make grating couplers using films of CW-HPA and W-IPA.

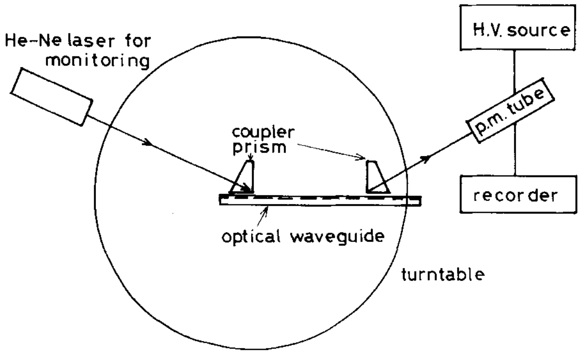


Figure 1 Arrangement for measuring characteristics of OWGs. Abbreviations: H.V., high voltage; P.M., photomultiplier.

RESULTS AND DISCUSSION

Preparation of the thin films of CW-HPA and W-IPA

The relation between the spin speed and the thickness of the dried films of W-IPA is shown in Fig. 2; practically the same relation was obtained for CW-HPA. Thinner films can be prepared with solutions with lower concentrations. Films thicker than 500 nm tend to crack after drying, as already pointed out.[7] Once dried at 80–120 °C for 1 h, the films with thicknesses less than 300 nm remained smooth, even when heated at 500 °C.

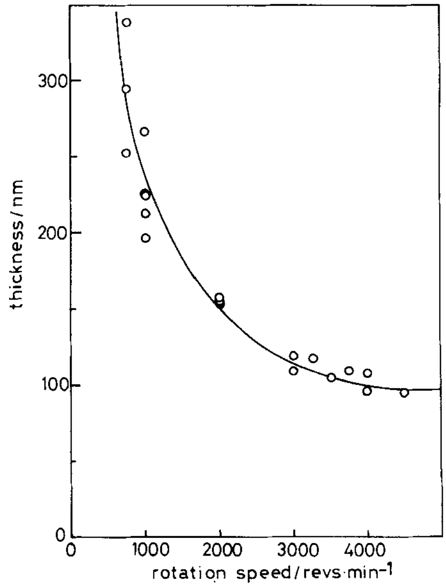


Figure 2 Relation between spin speed and thickness of the dried films of W-IPA. A 0.45 g portion of glassy W-IPA was dissolved into 1 cm^3 of water for the spin-coating solution.

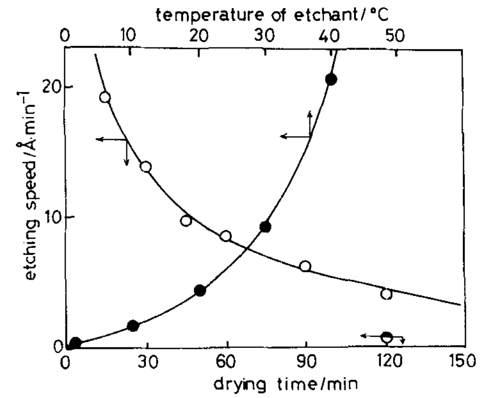


Figure 3 Etching speed of W-IPA films in water as a function of temperature of the etchant (water) and drying time (at 120 °C). The etching velocity of a film fired at 450 °C is also shown. CW-HPA gave practically the same characteristics.

Etching properties

The films, hardened by drying at 120 °C and/or by irradiation (the distance between the light source and the films was kept at 12 cm), were etched by immersing into etchants, and the resultant changes in thickness were measured. Etching was very slow in solutions containing acids such as HCl and H_2SO_4 although the latter was used as an etchant for CW-HPA and W-IPA in Ref. 5. Alkaline solutions etched the films so quickly that the films were severely damaged. Therefore we examined water as an etchant most extensively. The etching velocity in water for W-IPA is shown in Fig. 3 as a function of drying time and temperature of the etchant. The dependence of etching velocity on temperature is Arrhenius in nature, and gave 17.5 kcal mol^{-1} (73.5 kJ mol^{-1}) as the activation energy. Heating at higher temperatures, e.g. 450 °C, gave low etching speeds, as the figure shows. The films are supposedly converted into tungsten(II) oxide (WO_3) at this temperature according to Ref. 7. As shown in Fig. 4, drying and irradiation showed approximate additivity with respect to etching. We judged that the films were not etched when the interference color pattern showed no change after immersing the films in water for 3 min; this corresponds to a thickness change of less than 1–2 nm. We could not find large differences between CW-HPA and W-IPA with respect to etching properties.

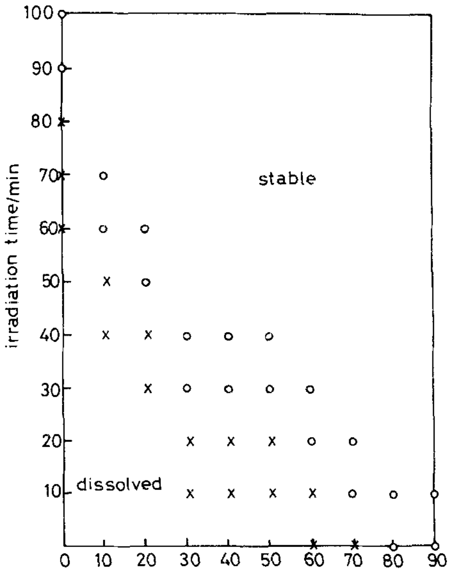


Figure 4 Effects of drying and irradiation on the etching property of W-IPA. The films were dried at 120 °C for 120 min prior to etching. In the figure, ○ shows the films were stable, and × denotes that their thickness decreased by at least 10–20 Å (1–2 nm) when immersed in water for 3 min at 30 °C. CW-HPA gave practically the same characteristics.

As an example of machining of these films, using the results shown in Fig. 4, we prepared a band OWG with a tapered structure, as Fig. 5(b) shows. The coated film was irradiated through a mask placed above the film at a minimal distance, as shown in Fig. 5(a). Slopes were obtained by etching because the etching velocity depended on the amount of irradiation, as Fig. 4 shows. The same structure can be prepared by immersing the coating in the etchant very slowly. These tapered

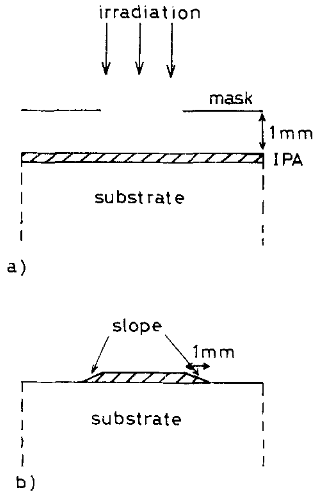


Figure 5 (a) Preparation of a band OWG having tapered velocity couplers at the both ends. (b) Structure of the band OWG obtained.

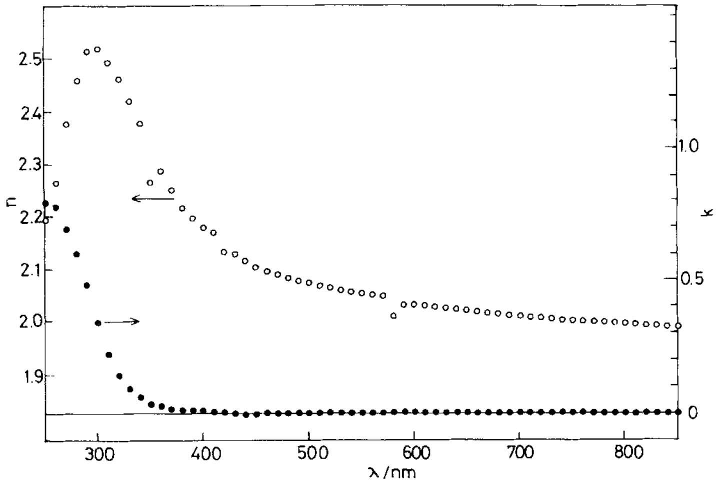


Figure 6 Real and imaginary components of the refractive index of W-IPA thin films as a function of wavelength. Data points with large scattering are supposedly due to inevitable errors in the measurements and the calculations associated with ellipsometry.

structures are useful for OWGs because they work as tapered velocity couplers which transfer light from one OWG to another.[2,9]

Refractive index

Figure 6 shows real and imaginary components of complex refractive index of W-IPA dried at 120 °C for 90 min. CW-HPA gave practically the same result. The imaginary index (*k*) in the figure shows that the films of W-IPA (and CW-HPA) are almost transparent in the visible wavelength regions except for the large absorption below 350 nm. Small finite *k* values were obtained in the wavelength regions of 0.4–0.8 μm, but this is probably because the analysis was based on a one-layer model. More exact dependence of *n* and *k* on wavelength will be obtained, for instance, by considering that the silicon substrate may have a natural SiO_2 layer.

The real index (*n*) was 2.0–2.5 in the wavelength region examined, e.g. 2.03 at 633 nm. It is surprising that films cured at such low temperatures (*ca* 100 °C) give such high *n* values. For instance, *n* of spin-coated $FePO_4$ films dried at 120 °C is 1.72,[1] and that of SiO_2–TiO_2 films fired at 500 °C is 1.8 at most.[4] TiO_2 films prepared by the sol–gel method can have *n* as high as 2.0, but they also need high firing temperatures, and moreover they are polycrystalline.

The films of W-IPA and CW-HPA showed large changes in *n* when dried or irradiated. As Fig. 7 shows, *n* changed from 1.67 (as-deposited film) to more than 2.0 by drying, and to 1.72 by irradiation; the probe light used was a helium–neon laser (633 nm) in these measurements. This shows that *n* increases as water and oxygen are released from the films,[7] particularly when heated. Carbon heteroatoms in CW-HPA are seemingly not important with respect to the high *n* values because the difference between CW-HPA and W-IPA was very small. The effect of irradiation on *n* was much less than that of drying. Moreover, *n* increased up to more than

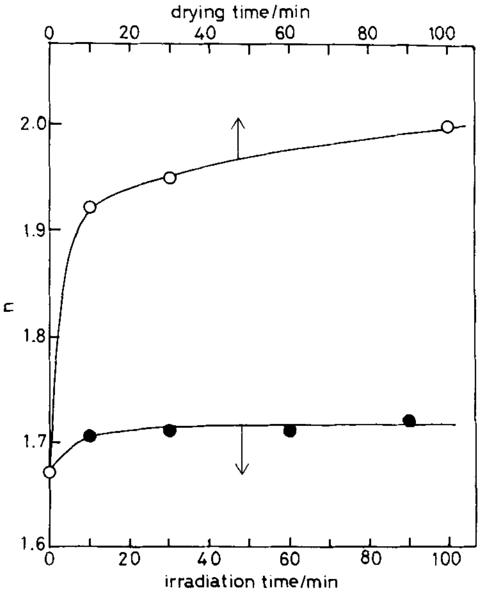


Figure 7 Dependence of the refractive index of W-IPA on drying time (120 °C) and irradiation time.

2.0 by drying the irradiated films. These findings suggest that irradiation causes mainly polymerization of W-IPA and CW-HPA, and not much release of water and oxygen. In addition, *n* increased by *ca* 0.2 when the films were heated to 450 °C. In this case, the films were supposedly converted into WO_3.

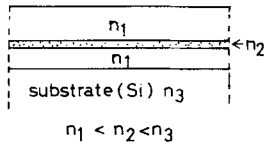
Optical waveguides (OWGs)

Amorphous films with high *n* values are interesting from the viewpoint of OWGs. We may be able to use them to fabricate thin-film OWGs and grating couplers with high diffraction efficiency. We tested thin-film OWGs of CW-HPA and W-IPA first. A thin film of these compounds coated onto a glass slide or an acrylic resin plate was placed on a pulsed motor-driven turntable, and efforts were made to introduce a helium–neon laser beam into the film through a coupler prism (cf. Fig. 1). We observed a guided mode only for films coated onto the plastic plate. The guided mode, however, was unstable because the film on the plastic plate degrades gradually. This is probably because film adhesion is weak.

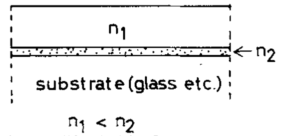
We cannot explain thoroughly, at this stage, the reason why we could not observe guided modes with the films coated onto the glass substrates. The films seem sufficiently transparent at 633 nm (cf. Fig. 6) as evidenced by the fact that the films coated onto a glass OWG gave little attenuation. This supports the view that the degree of transparency, is sufficient because attenuation of the guided light due to the films should be enhanced approximately 100-fold as compared with an absorption measurement employing normal incidence of monitoring light.[2] It may be possible, however, that the films exhibit minimal light absorption at this wavelength considering that they show photochromism when irradiated with UV light in the presence of reducing regents such as alcohols and water.[11] Even small absorption by the film leads to a large attenuation of the guided light when this is totally confined to the thin-film OWG. Enhancements in absorption are 10^4 times larger than those of usual absorption measurements. Hence, they are 10^2 times larger than that for the film on the glass OWG.[2]

Therefore, we constructed a band OWG with tapered velocity couplers shown in Fig. 5. In this structure, the laser beam is introduced from the thick-OWG part (glass OWG here) and is transferred into the thin-film part through the tapered region because of the adiabatic transition of light.[2] Thus, we can reduce the attenuation of the guided light by employing a small band width (2 mm here). We indeed observed transfer of the guided light from the glass OWG to the thin-film OWG and back again. The guided light was, however, largely attenuated; hence, CW-HPA and W-IPA are not good for thin-film OWGs on glass substrates.

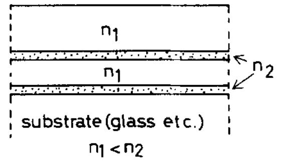
We therefore next tested OWG structures as shown in fig. 8. The OWG shown in Fig. 8(a) is an ARROW (Antiresonance Reflection Optical Waveguide) device.[12] Several modified versions can be envisioned as depicted in Figs 8(b) and 8(c).[3] These OWGs are transparent while the original type ARROW is not, because the silicon substrate used in this OWG reflects in the visible wavelength region. In addition, the bottom thin film with higher refractive index in the modified ARROW-2 [Fig. 8(c)] can be replaced with a highly reflective metal film if necessary. The guided light propagating in the upper layer of these OWGs is reflected at the interface between the upper layer and the clad layer with high *n*. The efficiency of the reflection is so large that there is little attenuation (leakage to the substrate in this case) of the guided light. We need thin films with high *n* in these ARROW-type OWGs, such as is possible with the CW-HPA and W-IPA films.



a) original type ARROW

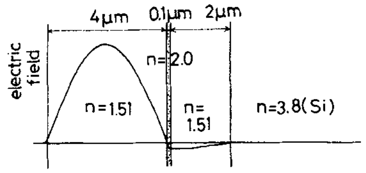


b) modified ARROW-1

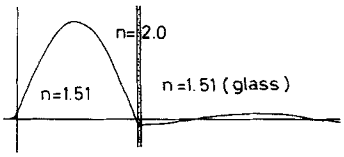


c) modified ARROW-2

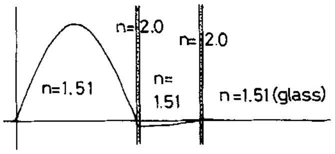
Figure 8 An original type of ARROW (Antiresonance Reflection Optical Waveguide) (a), and its modified types (b) and (c).



a) original type ARROW



b) modified ARROW-1



c) modified ARROW-2

Figure 9 Electric field distribution in the different OWG structures shown in Fig. 8. All in the thin films with $n = 2.0$ are 0.1 μm in thickness.

Differences between the OWGs shown in Fig. 8 are demonstrated in Fig. 9 in terms of the calculated electric field distributions in the waveguide structures. Numerical solutions of the wave equations were obtained using the Runge–Kutta–Gill method. We can see that the original ARROW type has negligible electric field in the substrate (silicon) and, hence, it shows little loss of the guided light. This is largely because of the high reflectivity at the surface of silicon; note that a difference in *n* between the guiding layer and the substrate silicon is very large. The modified ARROW-1 has a considerable electric field in the substrate, but its magnitude is much less than that in the waveguiding layer. In the modified ARROW-2, the electric field in the substrate is very small, suggesting that a loss of guided light in this OWG is also small.

We employed the modified ARROW-1 here just to demonstrate the validity of the idea. CW-HPA or W-IPA was spin-coated (*ca* 0.1 μm in thickness) onto a glass substrate or an acrylic resin plate, and dried. The photohardening resin was spin-coated onto the sample (*ca* 4 μm in thickness), followed by hardening with UV irradiation. We observed one guided mode propagating in the upper layer; however, the guided mode showed relatively large leakage to the substrate. This leakage is due to the simple structure of the modified ARROW-1 as shown above, and can be improved by employing the other ARROW structures.

Diffraction gratings

Diffraction gratings are important components of OWGs. They are used to couple the light beam into and out of the OWGs, and/or to split the guided light in the OWG plane. It has also been shown that the grating couplers work as very sensitive chemical sensors,[4] where a master grating was pressed onto thin films of TiO_2–SiO_2 mixtures when they are still soft. This embossing technique was used to fabricate replica gratings from the thin films of CW-HPA and W-IPA.

The master grating (*ca* 1 cm × 1 cm in size) was placed on the as-coated films on glass substrates and pressed using a vice. A silicone rubber sheet was placed between the sample and the vice plane to avoid breaking samples. The time required for pressing to obtain a good replica was not more than 10 s. The embossed samples were dried at 120 °C to harden the films. We can leave only the replica gratings by hardening the desired part with UV irradiation and by removing the other part with etching. This is one of the advantages of the use of CW-HPA and W-IPA. That is, etching properties of SiO_2–TiO_2 films mixtures[4] do not depend on irradiation, and thus, it is difficult to make these patterned structures with them. Diffraction efficiency was sufficiently high, and the grating indeed worked as a coupler when fabricated onto a glass OWG. We can utilize the high *n* values of these grating materials in several ways. For instance, the efficiency of coupling may be increased when used for OWGs with high *n*, and the sensitivity of the grating chemical sensor[4] may be enhanced.

In addition, in principle we can make gratings from CW-HPA and W-IPA with a holographic technique, electron beam exposure and so on. Although, the sensitivity of these materials to radiation is reportedly not as high as organic photoresists, it has been shown that addition of niobium or tantalum significantly increases the sensitivity.[11]

REFERENCES

1. Sloper, A N and Flanagan, M T *Electron Lett.*, 1988, 24: 353
2. Itoh, K *Photochemistry* (in Japanese), 1990, 14: 69

3. Itoh, K. Niikura, H, Okamoto, T, Wakita, S and Murabayashi, M *Bulletin of the Institute of Environmental Science and Technology, Yokohama National University*, 1991, 17: 45
4. Heuberger, K and Lukosz, W *Appl. Optics*, 1986, 25: 1499
5. Okamoto, H, Iwayanagi, T, Mochiji, K, Umezaki, H and Kudo, T *Appl. Phys. Lett.*, 1986, 49: 298
6. Kudo, T, Okamoto, H, Matsumoto, K and Sasaki, Y, *Inorg. Chim. Acta*, 1986, 111: L27
7. Yamanaka, K, Okamoto, H, Kidou, H and Kudo, T *Jpn. J. Appl. Phys.*, 1986, 25: 1420
8. For instance, Findakly, T *Opt. Eng.*, 1985, 24: 244
9. Itoh, K and Madou, M *J. Appl. Phys.*, 1991, 69: 7425
10. For instance, Yoshiike, N and Kondo, S, *J. Electrochem. Soc.*, 1984, 131: 2600
11. Itoh, K, Okamoto, T, Wakita, S and Murabayashi, M Japanese Patent pending; Itoh, K, Okamoto, T, Wakita, S, Murabayashi, M To be published
12. Duguay, M A, Kokubun, Y, Koch, T L and Pfeiffer L *Appl. Phys. Lett.*, 1986, 49: 13
13. Ishikawa, A, Okamoto, H, Miyauchi, K and Kudo, T *Denki Kagaku*, 1988, 56: 538