Growth of high quality ZnO thin films at low temperature on Si(100) substrates by plasma enhanced chemical vapor deposition

B. S. Li, Y. C. Liu, D. Z. Shen, Y. M. Lu, J. Y. Zhang et al.

Related Articles

Mixed Magnesium and Zinc Oxide Prepared by Co-precipitation and Analyzed by XPS
Surf. Sci. Spectra 19, 13 (2012)

Band alignment of zinc oxide as a channel layer in a gate stack structure grown by plasma enhanced atomic layer deposition
J. Vac. Sci. Technol. B 30, 051807 (2012)

Aluminum-doped zinc oxide formed by atomic layer deposition for use as anodes in organic light emitting diodes
J. Vac. Sci. Technol. A 31, 01A101 (2013)

Formation of zinc oxide films using submicron zinc particle dispersions
J. Vac. Sci. Technol. B 30, 041805 (2012)

In situ thickness and temperature measurements of CdTe grown by molecular beam epitaxy on GaAs substrate
J. Vac. Sci. Technol. B 30, 041203 (2012)

Additional information on J. Vac. Sci. Technol. A

Journal Homepage: http://avspublications.org/jvsta

Journal Information: http://avspublications.org/jvsta/about/about_the_journal

Top downloads: http://avspublications.org/jvsta/top_20_most_downloaded

Information for Authors: http://avspublications.org/jvsta/authors/information_for_contributors

Growth of high quality ZnO thin films at low temperature on Si(100) substrates by plasma enhanced chemical vapor deposition

B. S. Li, Y. C. Liu,[a] D. Z. Shen, Y. M. Lu, J. Y. Zhang, X. G. Kong, and X. W. Fan
Open Laboratory of Excited State Processes, Chinese Academy of Sciences, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 1-Yan An Road Changchun 130021, People's Republic of China

Z. Z. Zhi
Institute of Theoretical Physics, Northeast Normal University, Changchun 130024, People's Republic of China

High quality ZnO thin films with a *c*-axis-orientated wurtize structure have been grown on a Si(100) substrate by plasma enhanced chemical vapor deposition using a zinc organic source $[Zn(C_2H_5)_2]$ and carbon dioxide (CO_2) gas mixture at low temperature. The dependence of ZnO thin-film quality on the gas flow rate ratio of $Zn(C_2H_5)_2$ to CO_2 (GFRRZC) is studied by x-ray diffraction (XRD), optical transmission spectra (OTS), and photoluminescence spectra (PL). The optical properties show that the GFRRZC has an obvious effect on the band gap of ZnO films. The relationship between the quality of the ZnO thin films and the substrate temperatures is also studied by XRD and PL spectra. The XRD spectra show that the full width at half maximum (FWHM) of the diffraction peak at 34.42° of (0002) oriented ZnO is 0.25° at the optimized condition, indicating the formation of high quality ZnO films. The PL spectra show a strong excitonic emission at about 3.26 eV without the emission around 2.5 eV related to deep-level defects, implying the formation of the stoichiometric ZnO thin films. The smallest FWHM of the PL spectrum of a ZnO thin film is 111 meV at room temperature. © *2002 American Vacuum Society.* [DOI: 10.1116/1.1430427]

I. INTRODUCTION

Recently much attention has been paid to short wavelength lasers for use in high density information storage.[1–3] It is widely accepted that ZnO is the most promising material for realizing an ultraviolet laser at room temperature due to its wide direct band gap ($Eg = 3.3$ eV) with a large excitonic binding energy of 60 meV at room temperature.[3–5] To obtain high quality ZnO thin films, a variety of techniques may be used such as molecular-beam epitaxy,[6,7] metalorganic chemical vapor deposition, (MOCVD),[8] magnetron sputtering,[9,10] and pulsed laser deposition[11] for example. In the present article, plasma-enhanced chemical vapor deposition (PECVD) is employed to prepare ZnO thin films using a zinc organic source $Zn(C_2H_5)_2$ and CO_2 gas mixtures.

PECVD has several advantages in preparing ZnO thin films. The quality of the thin film can be improved by a film densification process induced by plasma bombardment and ultraviolet irradiation.[12] Furthermore, the low energy plasma can enhance the interface reaction. The $Zn(C_2H_5)_2$ and CO_2 are decomposed by high energy electrons in the plasma. Thus, the growth can be carried out at low temperature, even at room temperature. The growth at low temperature will reduce the strain effect caused by the different thermal expansions of the deposited layer and the substrate.

There is much interest in obtaining materials on Si substrates to realize optoelectronic integration. However, to our knowledge, there are few papers dealing with the growth of ZnO thin films on a Si substrate,[13–16] in particular, the growth of ZnO thin films on a Si substrate by PECVD. The growth of ZnO thin films on Si substrates using PECVD has an obvious advantage in that the plasma may remove the oxide layer on the Si surface, which is crucial when preparing high quality ZnO thin films. In this article, two sets of samples have been successfully grown to study the substrate temperature and the effect of the gas flow rate ratio of $Zn(C_2H_5)_2$ to CO_2 (GFRRZC) on the sample quality. The properties of the ZnO thin films are studied employing x-ray diffraction (XRD), optical transmission spectra (OTS), and photoluminescence (PL) spectra.

II. EXPERIMENTAL PROCEDURE

Figure 1 is the schematic diagram of the PECVD system. The flow rate of the two gases is controlled by different gas flowmeters. The gas flow rate of diethylzinc is controlled by adjusting the gas flow rate of hydrogen due to the low vapor pressure of $Zn(C_2H_5)_2$. The Si substrates are chemically treated by a standard Radio Corporation of America cleaning process[17] before being loaded into the growth chamber which has a background pressure of less than 4×10^{-4} Pa. After the argon and hydrogen are let into the chamber, the Si substrate is heated to a fixed temperature, which is monitored by a cuprum-constantan thermocouple. Then, the argon and hydrogen plasma induced by the rf field of 13.56 MHz is conducted in the chamber for 15 min to remove the oxide layers. The diethylzinc source is packaged in a steel cylinder
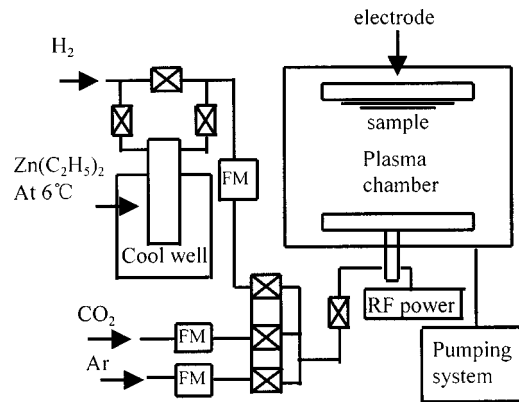

FIG. 1. Schematic diagram of the PECVD.

cool well and is kept refrigerated at 6 °C by a CW-1 type fine controlled temperature semiconductor device.

Generally, both the gas flow rate ratio and the substrate temperature will influence the sample quality. To clarify the two effects and to find the optimal growth conditions, two series of samples have been grown. The pressure in the chamber varied from 80–100 Pa during the GFRRZC experiment, and the pressure was held at 120 Pa in the changing-temperature experiment. The detailed growth conditions are listed in Tables I and Table II.

The crystalline quality of the ZnO layers was examined by XRD using a rotating anode x-ray diffractometer with Cu $K\alpha$, radiation of 1.54 Å. The OTS were measured by a UV-360 Recording Spectrophotometer (Shimadzu) at room temperature. A deuterium lamp was the light source with the wavelength range of 200 to 460 nm. The signals were detected by an R_{456}-type photoelectric multiplier with a high resolution of 0.1 nm. The PL spectra were measured using an UV Labran Infinity Spectrophotometer (J-Y Company, French) excited by a continuous He–Cd laser with a power of 30 mW and detected by a charge coupled device camera with a high resolution of 0.04 nm.

III. RESULTS AND DISCUSSION

A. Dependence of ZnO thin-film quality on the GFRRZC

To make the GFRRZC effect obvious, our samples were grown at the fixed substrate temperature of 180 °C. Figures 2(a)–2(d) shows the XRD spectra of the ZnO thin films prepared by PECVD with different GFRRZCs. When the

TABLE I. Deposition conditions of ZnO thin films with the gas flow ratio of $Zn(C_2H_5)$ to CO_2 (GFRRZC).

| Sample	GFRRZC	(rf) power (W)	Temperature of the substrate (°C)	Gas flow rate of argon (sccm)
A	1:0.5	35	180	4
B	1:1	35	180	4
C	1:2	35	180	4
D	1:3	35	180	4

TABLE II. Deposition conditions of ZnO thin films with different substrate temperatures.

Sample	Temperature of the substrate (°C)	(rf) power (W)	GFRRZC	Gas flow rate of argon (sccm)
A	60	35	4:5	4
B	100	35	4:5	4
C	140	35	4:5	4
D	180	35	4:5	4
E	230	35	4:5	4

GFRRZCs are 1:0.5 and 1:1, there are four diffraction peaks, as shown in Figs. 2(a), and 2(b), indicating multiorientation. When the GFRRZC is increased to 1:2 the (0002) diffraction peak dominates the spectrum with very weak diffractions from the (1020) and (1030) orientations. A preferred (0002) orientation ZnO thin film is obtained when the GFRRZC is 1:3. Additionally, with increasing CO_2, the full width at half maximum (FWHM) of the diffraction peak at 34.42° of (0002) oriented ZnO becomes smaller. FWHMs of samples A, B, C, and D are 0.57°, 0.47°, 0.27° and 0.25°, respectively. According to the Scherrer formula:[18]

$$d = 0.94\lambda/B \cos\theta, \qquad (1)$$

where d, λ, θ, and B are the mean grain size, the x-ray wavelength of 1.54 Å, Bragg diffraction angle, and the linewidth at half maximum of the peak at around 34.42°, respectively. The mean grain sizes of samples A, B, C, and D are 15 nm, 18 nm, 32 nm, and 35 nm, respectively. Because oxygen ions or radicals result from the decomposition of CO_2, increasing the CO_2 supply will create more oxygen ions and atoms. Thus, there will be enough oxygen ions to react with the zinc ions and form ordered ZnO thin films. However, if the sub-
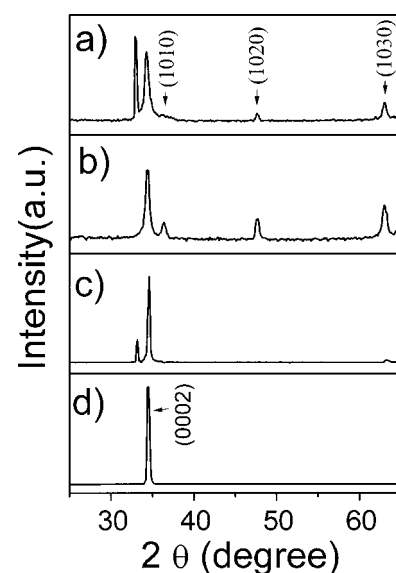
FIG. 2. XRD patterns of the ZnO thin films grown on Si (100) substrates under the different gas flow rate ratio of $Zn(C_2H_5)_2$ to CO_2 (GFRRZCs). (a) 1:0.5, (b) 1:1, (c) 1:2, and (d) 1:3.
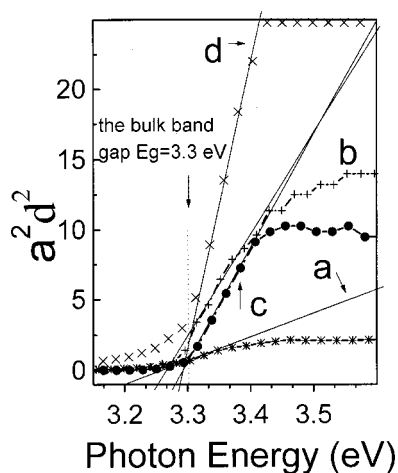
FIG. 3. Square of the absorption coefficient of ZnO thin films grown under the different GFRRZCs. (a) 1:0.5, (b) 1:1, (c) 1:2, and (d) 1:3.

FIG. 4. PL spectra of ZnO thin films grown at different GFRRZCs. (a) 1:0.5, (b) 1:1, (c) 1:2, and (d) 1:3.

strate temperature is fixed at 230 °C, the ZnO thin films show (0002) preferred orientation with all GFRRZCs. This will be discussed later.

The optical character of ZnO thin films is studied by transmission spectra. Here, we employ the characteristic function:[19]

$$(\alpha d)^2 \propto h\nu - E_g \tag{2}$$

to calculate the band gap energy, where $h\nu$ is the energy of photons, and E_g is the bulk band gap. α is the absorption coefficient which can be deduced from the transmission spectra with scattering from the film surface being neglected. The band gap of ZnO thin films is evaluated by extrapolating the linear part of the curve to intercept the energy axis. With increasing carbon dioxide, the calculated band gap E_g increases and approaches the bulk band gap as shown in Fig. 3. We believe the smaller band gap energy is caused by defects which exist between the grain surfaces because the films are polycrystalline. The absorption spectrum can be interpreted as a combination of absorption from the band gap states and the defect states below the band gap. The larger the number of defect states, the smaller the calculated band gap. This also can be proved by the slope of the absorption edge of the spectra. Here, we find the larger the slope, the larger the calculated band gap. We know the direct band gap semiconductor will have a very steep absorption edge because of its large density of states (DOS). However, the absorption of the indirect gap semiconductor or defects is much less steep due to their smaller DOS. So the increased absorption of the defects will make the absorption edge less steep. The absorption spectra are consistent with the results from XRD. With the increase of the CO_2 flow rate, the crystal quality and the grain size are improved. Thus, a reduction in the defect states will cause a steeper absorption edge.

Figure 4 is the PL spectra of ZnO thin films with different GFRRZCs measured at room temperature. Only the UV band emission can be observed. With the GFRRZCs increasing from 1:0.5 to 1:3, the FWHMs of the PL spectra become narrower. The FWHMs of the PL spectra of the samples A,
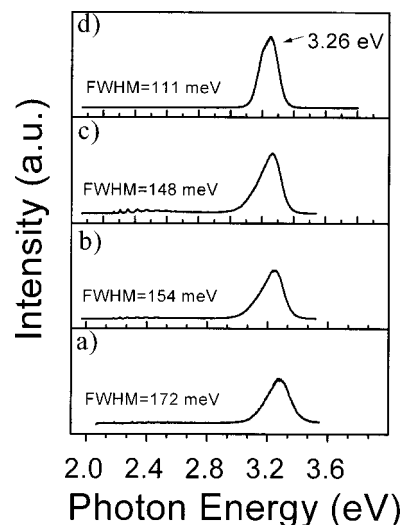
B, C, and D are 172 meV, 154 meV, 148 meV, and 111 meV, respectively. With the increase of CO_2, the orientation of the ZnO thin films, as well as the grain size, is improved. So the FWHMs of the PL spectra become narrower with the increase of intensity of the UV band emission, which comes from free exciton recombination.[20–22] Another interesting characteristic of the PL spectra is that no deep level emissions related to oxygen vacancies can be observed, even when there is a deficiency in the oxygen supply. Perhaps this is due to the fact that oxygen vacancies can be terminated by the excited hydrogen, which is helpful in obtaining the UV emission.

B. Effect of the substrate temperature on the film quality

Figures 5(b)–5(e) shows the XRD of the ZnO thin films prepared by PECVD at different temperatures with a fixed gas flow rate ratio of $Zn(C_2H_5)_2$ to CO_2 (GFRRZC) of 4:5. At a low substrate temperature, the ZnO thin films are polycrystalline with different orientations, as shown in Figs. 4(b) and 4(c). When the growth temperature reaches 170 °C, the diffraction peak of (0002) ZnO makes a dramatic increase. A preferred orientation of (0002) is realized when the growth temperature reaches 230 °C, as shown in Fig. 2(e). Moreover, the FWHM of (0002) ZnO at 34.42° decreases significantly with increasing substrate temperature. The FWHMs of samples B, C, D, and E are 0.41°, 0.44°, 0.29° and 0.26°, respectively. According to the Scherrer formula,[18] the mean grain sizes of the samples B, C, D, and E are about 21 nm, 20 nm, 30 nm, and 33 nm, respectively. The quality of the ZnO thin films is improved as the substrate temperature increases. The temperature dependence of the film quality can be interpreted mainly by the mobility and diffusion of the reactants. The reactants are decomposed by the plasma and are adsorbed on the substrate and diffuse into the substrate surface to form ZnO films. However, at low temperature, the radicals with low surface mobility will be located at different
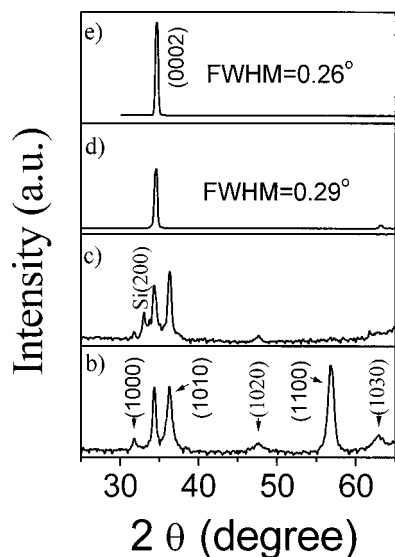
FIG. 5. XRD patterns of the ZnO thin films grown on Si (100) substrates prepared at different growth temperatures: (b) 100 °C, (c) 140 °C, (d) 170 °C, and (e) 230 °C.

FIG. 6. PL spectra of ZnO thin films prepared at different growth temperatures: (a) 60 °C, (b) 100 °C, (c) 140 °C, (d) 170 °C, and (e) 230 °C.

positions within the substrate. The ambient gases are also adsorbed in the films, limiting the mobility of the reactants, and preventing further growth of grains. Thus, the initial crystal nucleus tends to grow in the direction of available reactant flux. Additionally, if the thermal energy supplied by substrate is insufficient, the following chemical reaction can not take place:
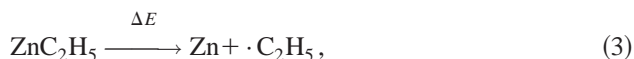
$$ZnC_2H_5 \xrightarrow{\Delta E} Zn + \cdot C_2H_5, \qquad (3)$$

where the ΔE is the thermal active energy required for the $\cdot C_2H_5$ radical to be released from the substrate. Thus, at low temperature, ZnC_2H_5 is embedded in the film and adversely affects the film quality. All of these factors will lead to different orientations of crystal grains and the formation of polycrystalline films. As the substrate temperature is increased, the mobility of reactants is increased and the gas product will be released from the substrate. The grain size may then increase and the film becomes homogeneous. If the ZnO thin films are prepared at room temperature, the films will have random orientations and the grain sizes will be small.

Figure 6(a)–6(e) shows the PL spectra of the ZnO thin films prepared by PECVD at different temperatures with a fixed GFRRZC of 0.8 measured at room temperature. The FWHM of the UV band that comes from free exciton recombination becomes narrower with the increase of substrate temperature. At 60 °C, shown in Fig. 6(a), the UV emission gives a broad peak at 3.43 eV. The blue shifted emission is caused by the quantum confinement effect due to the small size of ZnO. At low deposition temperature, the initial crystal nucleus tends to grow in the direction of available reactant flux due to the low mobility of radicals, so the grain sizes are small and the distribution of the grain size is large. At high temperatures, the grain size becomes larger and homoge-
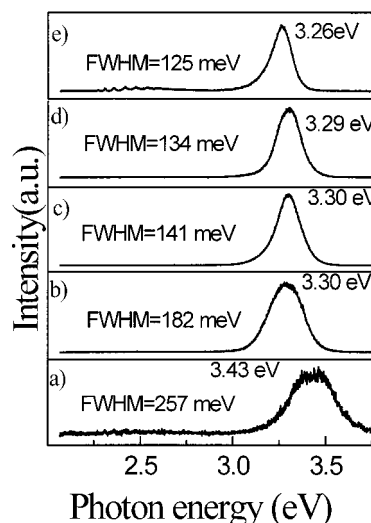
neous, so the FWHMs of the PL spectra become narrower and the peaks of the PL spectra have a redshift. The line-shape of the PL spectra shows an asymmetric structure on the low energy side, as shown in Figs. 4 and Fig. 6, which is caused by defects.[23] These defects exist at the grain and interface boundary between the substrate and epitaxy. The most important property of the PL spectra of ZnO thin films grown by PECVD is with a strong UV band emissions but without the deep level emission around 2.5 eV at room temperature, indicating a stoichiometric ZnO thin film. It is well known that the binding energy of an oxygen molecule is 5.16 eV, and conventional technology can not break O_2 into active oxygen atoms, causing the ZnO thin films to have many oxygen vacancies. In our experiment, the ZnO thin films are formed in the plasmas. The reactive zinc ions or atoms react directly with active oxygen ions or atoms obtained from CO_2 decomposed by plasma. Thus, it is easy to obtain stoichiometric films.

IV. CONCLUSIONS

ZnO thin films on a Si(100) substrate were prepared by PECVD from the gas mixture of diethylzinc and carbon dioxide at a low temperature (180 °C). The optimized GFRRZC is 1:3 deduced from the XRD, OTS, and PL spectra. The optimized substrate temperature is 230 °C as concluded from the XRD and the PL spectra. The plasma is crucial for the growth of ZnO thin films on a Si substrate. One reason is that it may remove the native oxide layer on the Si surface; another is that it supplies a sufficient number of active oxygen ions or atoms. By using this technique it is easy to form stoichiometric ZnO thin films.

ACKNOWLEDGMENTS

[1] M. A. Haase, J. Qiu, J. M. Depuydt, and H. Cheng, Appl. Phys. Lett. **59**, 1272 (1991).

[2] S. D. Lester, F. A. Ponce, M. Gcraford, and D. A. Steigerwald, Appl. Phys. Lett. **66**, 1249 (1995).

[3] R. F. Service, Science **276**, 895 (1997).

[4] Z. K. Tang, G. K. L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, Appl. Phys. Lett. **72**, 3270 (1998).

[5] K. K. Kim, J. H. Song, H. J. Jung, W. K. Choi, S. J. Park, J. H. Song, and J. Y. Lee, J. Vac. Sci. Technol. A **18**, 2864 (2000).

[6] D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, M. Y. Shen, and T. Goto, Appl. Phys. Lett. **73**, 1038 (1998).

[7] F. Siah, Z. Yang, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, J. Appl. Phys. **88**, 2480 (2000).

[8] K. Haga, F. Katahira, and H. Watanabe, Thin Solid Films **343**, 145 (1999).

[9] A. Hachigo, H. Nakahata, K. Higaki, S. Fujii, and S. Shikata, Appl. Phys. Lett. **65**, 2556 (1994).

[10] J. Hinze and K. Ellmer, J. Appl. Phys. **88**, 2443 (2000).

[11] X. W. Sun and H. S. Kwok, J. Appl. Phys. **86**, 408 (1999).

[12] Y. J. Kim and H. J. Kim, Mater. Lett. **21**, 351 (1994).

[13] K. Iwata, P. Fons, S. Niki, S. Niki, A. Yamada, K. Matsubara, T. Tanabe, and H. Takasu, J. Cryst. Growth **214**, 50 (2000).

[14] M. Joseph, H. Tabata, and T. Kawai, Appl. Phys. Lett. **74**, 2534 (1999).

[15] Z. X. Fu, B. X. Lin, G. H. Liao, and Z. Q. Wu, J. Cryst. Growth **193**, 316 (1998).

[16] A. Miyake, H. Kominami, H. Tatsuka, H. Kuwabara, Y. Nakanishi, and Y. Hatanaka, J. Cryst. Growth **214**, 294 (2000).

[17] W. Kern and D. A. Puotinen, RCA Rev. **31**, 187 (1970).

[18] W. T. Lim and C. H. Lee, Thin Solid Films **353**, 12 (1999).

[19] F. Demichelis, G. Kaniadakis, A. Tagliaferro, and Tresso, Appl. Opt. **26**, 1737 (1987).

[20] S. Miyamoto, Jpn. J. Appl. Phys., Part 1 **17**, 1129 (1978).

[21] D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Tao, M. Y. Chen, and T. Goto, Appl. Phys. Lett. **73**, 1083 (1998).

[22] S. Bethke, H. Pan, and B. W. Wessel, Appl. Phys. Lett. **52**, 138 (1988).

[23] Y. F. Chen, D. M. Bagnall, H. J. Kon, K. Park, K. Hiraga, and Z. Q. Zhu, J. Appl. Phys. **84**, 3912 (1998).