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Properties of Liquid-Phase Deposited Silica Films for Low-*k* Dielectric Applications

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Both the electrical and mechanical properties of silica thin films deposited by liquid phase deposition (LPD) have been evaluated in this study. Silica thin films have been prepared on glass surface by immersing it in a supersaturated Hexafluorosilicic acid (H_2SiF_6)-based solution at a low temperature of 50°C. The as-deposited LPD silica films exhibit a low dielectric constant (*k*) that varies from 1.7 to 2.7 depending on the film morphology and fluorine content of the film. Young's modulus of these films was measured in the range of 18.9–24.5 GPa by a nanoindentation technique. The combination of extremely low *k* and fairly high modulus made this low-temperature-processed LPD silica films a very promising candidate for an interlayer dielectric film for the next-generation semiconductor devices.

I. Introduction

With the increasing demands on reducing the feature size in microelectronics, problems including propagation delay, cross-talk noise, and power dissipation become significant and seriously degrade the performance of electronic devices.[1–3] Therefore, replacing the conventional silica that has a dielectric constant (*k*) value of 4.0 with low-*k* materials as dielectric interlayer in ultra large-scale integrated circuit (IC) is very critical and inevitable.[3–6]

Several approaches have been developed for lowering the *k* of silica films. Basically, the *k* can be reduced through a reduction in electronic polarization or through the introduction of porosity.[7] The introduction of porosity is widely studied due to the controllability of pore size and distribution in some deposition process, like sol–gel.[8–12] However, the high-porosity silica-based film is at the cost of mechanical strength, which makes the integration process more difficult and device performance less reliable. Therefore, introducing the fluorine ion (F), which has the least polarizability, into the silica film becomes a very promising means of achieving low-*k* silica. A variety of deposition techniques have been used to deposit silica films with F doping. Plasma-enhanced chemical vapor deposition introduced F into the silica film using a fluorine gas source, such as CF_4 and SiF_4.[13] In the sol–gel method, the F ions were introduced by using hydrofluoric acid (HF) as a catalyst.[9,11] The resultant F-doped silica films showed an obvious decrease in the *k* from both processing methods.

In our study, the silica films were prepared by the liquid phase deposition (LPD) technique[14–16] and the fluorine ion was introduced into the films through Hexafluorosilicic acid (H_2SiF_6). Both the electrical and mechanical properties of deposited LPD silica films were characterized. LPD-processed silica films have been reported to possess better electrical properties, such as lower leakage current, higher dielectric breakdown strength, and lower *k* than the CVD silica films, and tested and explored in processing of ICs, thin film transistors, waveguides, and solar cells.[14–19] Furthermore, the simplicity to process and low-temperature use in the processing make LPD silica very attractive not only for next-generation interlayer dielectric films, but also applications that cannot accommodate high-temperature processing and high manufacturing cost.

II. Experimental Procedure

The precursor was prepared by adding silicic acid powder ($SiO_2 \cdot xH_2O$) into a 3.2*M* H_2SiF_6 solution and dissolved by stirring overnight at 25°C. The residual powder was then removed by centrifugal separation. The films were prepared on the commercially available F-doped tin oxide (FTO)-coated glass (Hartford Glass Co. Inc., Hartford City, IN). Before immersing the substrate, the solution was diluted with DI water to desired concentration, and 0.005–0.01*M* boric acid (H_3BO_3) was added to facilitate the saturation of SiO_2 particle in the solution. Three samples with the different ratio of the H_2SiF_6 concentration to the H_3BO_3 concentration were prepared. Table I lists the details of the acid and their concentration ratio used for each sample in the order of an increasing deposition rate. All the deposition temperature was set at 50°C. In order to avoid the settlement of precipitated particles and their aggregates, the substrates were positioned vertically, and the deposition was conducted in a stepwise fashion, i.e., after every 0.5–1 h of heating, the precursor solution was drained and fresh precursor solution was filled.

The thickness of the film was measured by a profilometer (Dektac 8 Advanced Development Profiler, Veeco Instruments Inc., Plainview, NY). The morphology of the film was observed through scanning electron microscope (SEM) (Zeiss Supra 55, Jena, Germany). All the SEM images were taken with an accelerating voltage of 1–2 kV and a working distance around 5 mm. The SEM cross-section analyses were also conducted to further confirm the film thickness and structure. In addition, atomic force microscope (AFM) was used to observe surface roughness.

The mechanical properties of the as-deposited films were measured by a nanoindentation system (Hysitron TriboIndenter, Minneapolis, MN) with a standard Berkovich diamond indenter tip. In particular, Young's modulus was measured by the nanodynamic mechanical analysis (nanoDMA) method, which provides the mechanical properties as a function of time or displacement in a single indentation. The quasi-static load was set to increase in discrete steps up to a maximum value of 5000 μN to ensure the displacement into film could be significant enough to observe the substrate effect. The frequency of the superimposed sinusoidal loading was set at 50 Hz, and a dynamic load of 10 μN was used for all the LPD silica samples.

The capacitance and *k* of the films were obtained using metal insulator conductor ($Ag/SiO_2/FTO$-Glass) test structure. Silver dots with an area around 2 mm^2 were patterned on the top surface of the film; the bottom side of the film was in contact with

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Table I. Precursor Details and the Resultant Film Thickness and Roughness for Each Prepared Sample

Sample	Chemical concentration H_2SiF_6 (M)/H_3BO_3 (M)	Deposition rate (nm/h)	Film thickness (nm)	Surface roughness (nm)
LPD_S1	H_2SiF_6 (0.5)/ H_3BO_3 (0.01)	43	300±6	52.2±1.3
LPD_S2	H_2SiF_6 (2.0)/ H_3BO_3 (0.005)	82	575±20	59.7±1.8
LPD_S3	H_2SiF_6 (1.0)/ H_3BO_3 (0.005)	118	830±30	64.3±4.1

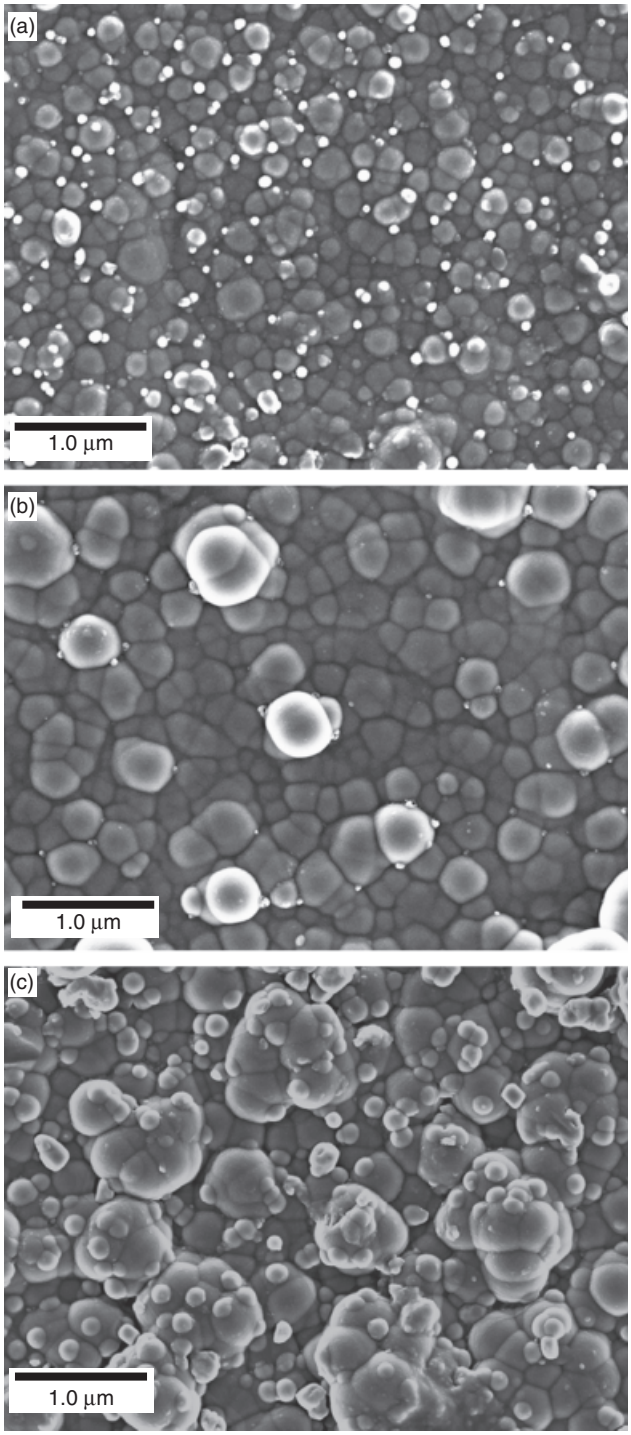

Fig. 1. Scanning electron micrographs of liquid phase deposited silica sample: (a) S1, (b) S2, and (c) S3.

the FTO coating, which served as the bottom electrode. The capacitance of the aforementioned metal–insulator–conductor structure was measured by using a HP 4284A LCR meter (Hewlett Packard, Santa Clara, CA) at a frequency of 1 kHz and 1 MHz. The k was then calculated from the capacitance, the film thickness, and the area of the metal electrode.

III. Results and Discussion

Figure 1 shows the SEM micrographs for the LPD-silica film grown on the FTO-coated glass substrate. It was found that a layer of dense silica film was obtained in all three deposition cases. Different morphologies, however, were developed due to the differences in the processing condition; more specifically, a different ratio of the H_2SiF_6 to the H_3BO_3 was added into the precursor. With 2.0M of H_2SiF_6 and 0.005M of H_3BO_3, uniformly distributed grain structure was obtained with few particles adsorbed onto the growing films (Fig. 1(b)). By decreasing the H_2SiF_6 concentration to 1.0M at the same H_3BO_3 concentration, the deposition rate increased, which may be attributed to the less etching effect from HF on the growing SiO_2 film during deposition. The grain structure was, however, much less uniform, got more aggregated and rougher, and had more number of particles adsorbed from bulk precipitation in precursor solution (Fig. 1(c)). AFM characterization of each film surface confirms this aspect, as listed in Table I.

By further reducing the H_2SiF_6 concentration to 0.5M, the deposition rate was, however, dramatically reduced due to more contribution from bulk precipitation, and so very slow deposition occurred with the same H_3BO_3 concentration. Therefore, the H_3BO_3 concentration was raised to 0.01M, and the film deposition occurred with very fine grain structure (Fig. 1(a)). In addition, much smaller particles obtained from bulk precipitation were adsorbed onto the growing film. This observation indicates that H_3BO_3 increases supersaturation of the precursor solution, and therefore promotes more homogeneous nucleation of SiO_2 particles in solution by scavenging the HF and generating water.[14] On the other hand, the H_2SiF_6 concentration controls more on surface reaction and grain structure through the number of nuclei formed. It is therefore critical to optimize the concentration ratio of H_2SiF_6 to H_3BO_3 to minimize aggregated particles on the growing film surface.

Figure 2 shows examples of indentation (reduced) modulus as a function of displacement from the nanoindentation tests conducted for S1, S2, and S3 samples. As shown in the plot, for all these samples, there is a gradual increase in indentation modulus with displacement, implying the substrate effect. In particular, the thinnest film S1 exhibited the highest modulus and the largest scattering of data, both of which decreased with the

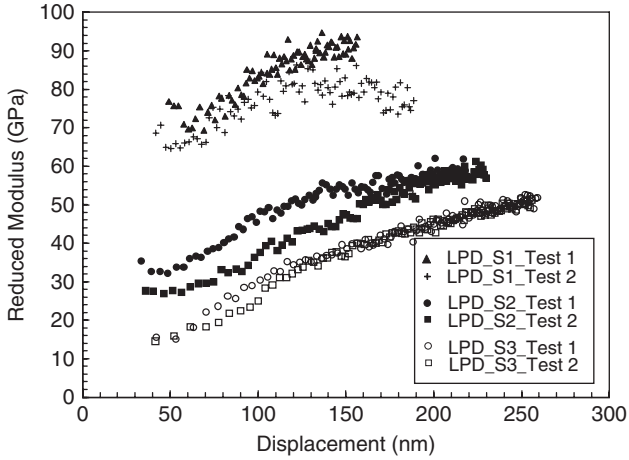

Fig. 2. Plot of reduced modulus as a function of displacement for liquid phase deposited (LPD) silica samples (two examples for each sample).

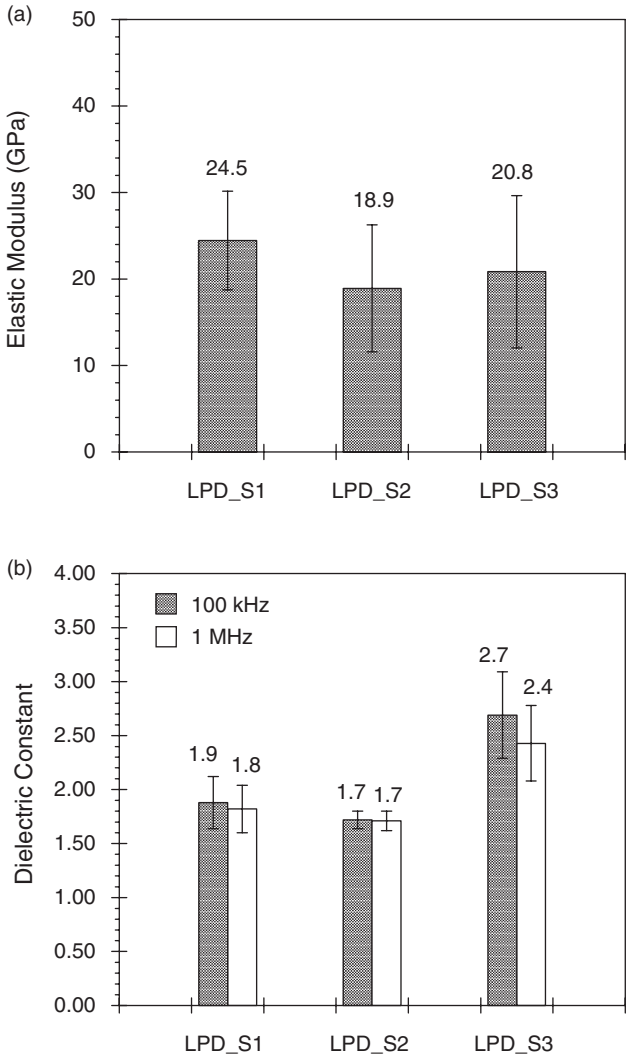

Fig. 3. Column chart presents the Young's modulus (a) and dielectric constant (b) for all the studied samples. Note that in part (b), the results from two frequencies (100 kHz and 1 MHz) are compared.

film thickness. Therefore, direct data reading was not feasible to obtain the "true" film modulus. One indentation standard (bISO/DIS 14577-4)[20] was adopted to obtain true Young's modulus from the film by extrapolating the indentation data to an infinite thickness. At least, four measurements were analyzed to determine the modulus of each sample. The results are shown in Fig. 3(a), where all three displayed similar elastic moduli around 18.9–24.5 GPa although the S1 sample exhibited the highest Young's modulus within the data error probably because of the highly dense, fine grain structure as shown in Fig. 1.

Figure 3(b) shows the k's measured at 100 kHz and 1 MHz with a precision LCR meter. All of the studied LPD silica films presented a relatively low k compared with most of the silica films fabricated by other techniques. As illustrated in the column chart, among all the LPD SiO_2 films, sample S2 exhibited the lowest k value of 1.7, which is very likely an outcome of the F content in the silica film because the H_2SiF_6 concentration for S2 was the highest among all the samples. Even though sample S3 was prepared with a higher H_2SiF_6 concentration than sample S1, the k of S3 was much larger than that of S1. The plausible explanation for this result is that sample S3 was prepared with the highest deposition rate, and so had little time to etch the Si–OH network with HF, resulting in less amount of F content incorporated into the film. This sample also has more data scattering due to rougher surface.

Table II summarizes the k and modulus of SiO_2 prepared by various methods from the literature,[21–24] compared with the values reported in this paper. The low k ($k<2.3$) along with sufficient mechanical properties ($E>18$ GPa) for S1 and S2 films makes the LPD-SiO_2 films suitable for a low-k film for such applications as in microelectronics, OLEDs, and flexible electronics. In addition, this SiO_2 film is generated at near room temperature without incorporating significant void structure. The dense film structure will be beneficial to provide a good thermal conduction path to dissipate the generated heat more efficiently.

IV. Conclusions

Both the electrical and mechanical properties of SiO_2 films deposited by the LPD method have been investigated in this study. By adjusting the chemical concentrations in the LPD precursor, film properties can be tuned accordingly. The as-deposited LPD silica films generally exhibit a low k from 1.7 to 2.7 depending on the processing condition and film morphology. An ultra low k value of 1.7 obtained is likely related to the high level of F content in the film. Young's modulus of these films varied from 18.9 to 24.5 GPa depending on the film roughness and structure. The remarkably low k and fairly high modulus LPD silica films achieved by this low-temperature process make it into a very promising candidate for low-k dielectric materials for semiconductor devices and flexible electronics.

Table II. Comparison of Dielectric Constant and Modulus of Liquid Phase Deposition (LPD) Silica Films from this Work with Literature Values

References	Dielectric constant	Deposition method	Modulus/measurement technique
Homma and Murao[15]	3.7–3.9	LPD	NA
Zhang and Boyd[8]	1.7	Photo-induced sol–gel processing	NA
Yu *et al.*[12]	2.0	Sol–gel processing	NA
He *et al.*[9]	1.65	Sol–gel method with catalyst HF	NA
Shen *et al.*[10]	~2.5	Dip-coating process	NA
Farrell *et al.*[22]	2.3	Evaporation-induced self-assembly (EISA)	NA
Zhen *et al.*[11]	1.67	Sol–gel method and spin coating technique	NA
Maruo *et al.*[21]	1.5–1.7	Sputtering	NA
Shen *et al.*[23]	3.09	PECVD	13.98 GPa/nanoindentation
Wang *et al.*[7]	~2.4	PECVD	~4 GPa/nanoindentation
Jung *et al.*[24]	2.55	Evaporation-induced self assembly (EISA)	13–14.4 GPa/nanoindentation
This paper	1.7–2.7	LPD with different "F" content and microstructure	18.9–24.5 GPa/nanoindentation

PECVD, plasma-enhanced chemical vapor deposition.

References

[1]M. E. Thomas, "The Future of Interconnects," *Solid State Technol*., **41** [2] 44 (1998).

[2]Y. Y. Jin, K. Kim, and G. S. Lee, "Preparation of Low Dielectric Constant Silicon Containing Fluorocarbon Films by Plasma Enhanced Chemical Vapor Deposition," *J. Vacuum Sci. Technol. B*, **19** [1] 314–6 (2001).

[3]K. Maex, M. R. Baklanov, D. Shamiryan, F. Lacopi, S. H. Brongersma, and Z. S. Yanovitskaya, "Low Dielectric Constant Materials for Microelectronics," *J. Appl. Phys*., **93** [11] 8793–841 (2003).

[4]M. Vasilopoulou, A. M. Douvas, D. Kouvatsos, P. Argitis, and D. Davazoglou, "Characterization of Various Insulators for Possible Use as Low-k Dielectrics Deposited at Temperatures below 200°C," *Microelectron. Reliab*., **45** [5–6] 990–3 (2005).

[5]M. Morgen, E. T. Ryan, J. H. Zhao, C. Hu, T. H. Cho, and P. S. Ho, "Low Dielectric Constant Materials for ULSI Interconnects," *Annu. Rev. Mater. Sci*., **30**, 645–80 (2000).

[6]S. J Martin, J. P Godschalx, M. E Mills, E. O Shaffer, and P. H Townsend, "Development of a Low-Dielectric-Constant Polymer for the Fabrication of Integrated Circuit Interconnect," *Adv. Mater*., **12** [23] 1769–78 (2000).

[7]Y. H. Wang, M. R. Moitreyee, R. Kumar, S. Y. Wu, J. L. Xie, P. Yew, B. Subramanian, L. Shen, and K. Y. Zeng, "The Mechanical Properties of Ultra-Low-Dielectric-Constant Films," *Thin Solid Films*, **462–463**, 227–30 (2004).

[8]J.-Y. Zhang and I. W. Boyd, "Low Dielectric Constant Porous Silica Films Formed by Photo-Induced Sol–Gel Processing," *Mater. Sci. Semicond. Process*., **3** [5–6] 345–9 (2000).

[9]Z. W. He, X. Q. Liu, D. Y. Xu, and Y. Y. Wang, "Effect of Annealing on the Properties of Low-k Nanoporous SiO_2 Films Prepared by Sol–Gel Method with Catalyst HF," *Microelectron. Reliab*., **46** [12] 2062–6 (2006).

[10]J. Shen, A. Luo, L. Yao, X. Lin, B. Zhou, G. Wu, and X. Ni, "Low Dielectric Constant Silica Films with Ordered Nanoporous Structure," *Mater. Sci. Eng. C*, **27** [5–8] 1145–8 (2007).

[11]C. M. Zhen, J. J. Zhang, Y. J. Zhang, C. X. Liu, C. F. Pan, and D. L. Hou, "Fluorinated Nanoporous SiO_2 Films with Ultra-Low Dielectric Constant," *J. NonCryst. Solids*, **354** [32] 3867–70 (2008).

[12]S. Yu, T. K. S. Wong, X. Hu, and K. Pita, "Sol–Gel Derived Mesoporous Silica Films Used as Low Dielectric Constant Materials," *Thin Solid Films*, **462–463**, 311–5 (2004).

[13]S. J. Ding, D. W. Zhang, J. T. Wang, and W. W. Lee, "Low Dielectric Constant SiO_2: C,F Films Prepared from $Si(OC_2H_5)_4/C_4F_8$/Ar by Plasma-Enhanced CVD," *Chem. Vap. Deposition*, **7** [4] 142–6 (2001).

[14]H. Nagayama, H. Honda, and H. Kawahara, "A New Process for Silica Coating," *J. Electrochem. Soc*., **135** [8] 2013–6 (1988).

[15]T. Homma and Y. Murao, "Properties of Liquid-Phase-Deposited SiO_2 Films for Interlayer Dielectrics in Ultralarge-Scale Integrated Circuit Multilevel Interconnections," *Thin Solid Films*, **249** [1] 15–21 (1994).

[16]J.-S. Chou and S.-C. Lee, "Improved Process for Liquid Phase Deposition of Silicon Dioxide," *Appl. Phys. Lett*., **64** [15] 1971–3 (1994).

[17]C. F. Yeh and C. L. Chen, "Controlling Fluorine Concentration and Thermal Annealing Effect on Liquid-Phase Deposited Sio_2–xFx Films," *J. Electrochem. Soc*., **142** [10] 3579–83 (1995).

[18]Y. Sakai, H. Norimatsu, Y. Saito, H. Inomata, and T. Mizuno, "Silica Coating on Plastics by Liquid Phase Deposition (LPD) Method," *Thin Solid Films*, **392** [2] 294–8 (2001).

[19]T. P. Niesen and M. R. De Guire, "Review: Deposition of Ceramic Thin Films at Low Temperatures from Aqueous Solutions," *Solid State Ionics*, **151** [1–4] 61–8 (2002).

[20]ISO/DIS 14577-4, "Metallic Materials—Instrumented Indentation Test for Hardness and Materials Parameters (Part 4: Test Method for Metallic and Non-Metallic Coatings)," International Organization for Standardization, 2005.

[21]T. Maruo, S. Tanaka, H. W. Hillhouse, N. Nishiyama, Y. Egashira, and K. Ueyama, "Disordered Mesoporous Silica Low-k Thin Films Prepared by Vapor Deposition Into a Triblock Copolymer Template Film," *Thin Solid Films*, **516**, 4771–6 (2008).

[22]R. A. Farrell, K. Cherkaoui, N. Petkov, H. Amenitsch, J. D. Holmes, P. K. Hurley, and M. A. Morris, "Physical and Electrical Properties of Low Dielectric Constant Self-Assembled Mesoporous Silica Thin Films," *Microelectron. Reliab*., **47** [4–5] 759–63 (2007).

[23]L. Shen, K. Zeng, Y. Wang, B. Narayanan, and R. Kumar, "Determination of the Hardness and Elastic Modulus of Low-k Thin Films and Their Barrier Layer for Microelectronic Applications," *Microelectron. Eng*., **70** [1] 115–24 (2003).

[24]S.-B. Jung, C.-K. Han, and H.-H. Park, "Electrical and Mechanical Properties of Surfactant-Templated Mesoporous Silica Thin Films Using Brig-76 Surfactant," *Appl. Surf. Sci*., **244**, 47–50 (2005). □