



BaTiO₃ Films by Low-Temperature Hydrothermal Techniques for Next Generation Packaging Applications

D. BALARAMAN, P.M. RAJ,* L. WAN, I.R. ABOTHU, S. BHATTACHARYA, S. DALMIA, M.J. LANCE,†
M. SWAMINATHAN, M.D. SACKS & R.R. TUMMALA

Packaging Research Center, Georgia Institute of Technology, Atlanta, GA 30332-0560, USA

Submitted March 4, 2003; Revised January 12, 2004; Accepted January 22, 2004

Abstract. This work reports synthesis, characterization and integration of sub-micron thick nano-grained barium titanate films on organic Printed Wiring Boards (PWB). Barium titanate films were synthesized on titanium foils at 95°C. SEM of films revealed 80 nm grains. The films were characterized using XRD, FTIR and Raman spectroscopy. As-synthesized films exhibited high capacitance densities and dielectric loss. The films were treated with oxygen plasma to reduce entrapped hydroxyl groups and this resulted in improved dielectric properties. The plasma treated films exhibited a capacitance density of 1 $\mu\text{F}/\text{cm}^2$ and a dielectric loss of 0.06. The high frequency dielectric properties were extracted from s-parameter measurements on CPW structures on these films and were found to be stable up to 8 GHz.

Keywords: embedded capacitors, decoupling, Raman, FTIR, dielectric constant, PWB, barium titanate, high frequency

1. Introduction

Integration of passive components like resistors, inductors and capacitors into the Printed Wiring Board remains a major barrier to realizing convergent miniaturized systems. Currently passives are manufactured as discrete components and soldered on the Printed Wiring Boards (PWB) using surface mount techniques. Integration of these passives into the board tremendously increases board area available for active devices thus increasing the functionality of microsystems. Among various passive devices, capacitors are the hardest to integrate owing to non-availability of material systems to cover the entire range of capacitances (0.1 pF–10.0 μF), used in today's microsystems. Polymer films, pure and ceramic-filled, can achieve capacitances only up to a few tens of nano-farads and hence are not suitable for decoupling applications that require

high k thin films. In addition to high dielectric constant, these films should exhibit low leakage currents and stable dielectric properties up to a few GHz.

It is well known that ferroelectric thin films can achieve high capacitance densities and low loss. The main drawback of ferroelectrics is their frequency-dependent dielectric properties. For example, barium titanate, depending on grain size, has been reported to show dielectric relaxation at frequencies as low as 1 GHz [1]. Dielectric relaxation is characterized by a drop in dielectric constant and an increase in dielectric loss at the characteristic relaxation frequency. Decreasing the grain size can increase the relaxation frequency but is usually accompanied by a decrease in dielectric constant due to reduction in tetragonality of barium titanate crystals. However, NEMI roadmaps [2] suggest that sub-micron thick films with a moderate dielectric constant of 300 are adequate to meet most of the decoupling capacitor requirements. Among different ceramic film synthesis techniques available today, some methods such as sol-gel processing require high temperatures (500°C) for crystallizing barium titanate and hence cannot be used on organic PWBs. Others like

*To whom all correspondence should be addressed. E-mail: raj@ece.gatech.edu

†Present address: Oak Ridge National Laboratory, Oak Ridge, TN-37831-6068, USA.

MOCVD require special vacuum chambers and hence are not economical for large area synthesis. Clearly novel thin film synthesis techniques are required to integrate decoupling capacitors on PWB.

In the past decade there has been tremendous interest in hydrothermal synthesis techniques which can yield crystalline barium titanate films and powders at temperatures less than 100°C. Several authors have reported synthesis of thin films by hydrothermal treatment of metallic titanium [3] and spun-on organic precursors of titanium [4]. Films synthesized from organic precursors are typically porous presumably because of low titanium content in the precursor films. Hence, the precursor films are densified at high temperatures (>300°C) prior to hydrothermal synthesis [5]. Furthermore, post-hydrothermal heat treatments may be required to eliminate entrapped hydroxyl groups which are known to deteriorate the dielectric properties of barium titanate films. Hence the process needs to be modified to enable integration on organic boards. Furthermore, high frequency electrical properties of hydrothermal films are not well characterized. This paper focuses on synthesis of low loss hydrothermal films, electrical characterization and integration on (PWB).

2. Experimental

2.1. Hydrothermal Synthesis

Hydrothermal synthesis of BaTiO₃ involves treating a suitable titanium source with Ba²⁺ ions in highly alkaline solution. The temperatures range from 25 to 250°C. The source of titanium can be an organic precursor like TIBE (titanium diisopropoxide bis(ethyl acetoacetate)), inorganic titanium compound like TiCl₄ or metallic titanium. In the preliminary studies, organic precursors (TIBE + Toluene, 1:1) and 1 μm thick evaporated titanium were examined and were found to result in porous films which did not yield any capacitance measurements. Throughout this current study, titanium foils have been used to demonstrate the ease of integration of hydrothermal films via standard PWB processes—lamination and lithography. These foils were laminated on to FR-4 using epoxy prepregs in a 50-ton vacuum hot-press. Prior to hydrothermal treatment, the foils were cleaned with acetone, followed by a descum process with oxygen plasma treatment.

2 M Ba(OH)₂ was found to be optimum concentration for hydrothermal synthesis from earlier studies.

Lower concentrations led to coarser grains while higher concentration resulted in precipitates at 95°C. The solution was prepared by dissolving barium hydroxide in boiling deionized (DI) water to eliminate dissolved carbon dioxide. The solution was then filtered into the reaction container. The pH of the solution was measured to be 13.5 at 95°C. The laminated foils were placed with the titanium facing down to prevent possible deposition of precipitates onto the titanium foil surface which could inhibit the hydrothermal reaction locally and resulting in poor yield i.e., smaller percentage of functional capacitors in a given area. Further, thinner foils were found to yield finer grains and denser microstructure resulting in better yield. Hence, 12.5 μm thick foils were used in the current study. The reaction was allowed to proceed for 24 hours. The hydrothermally treated samples were rinsed thoroughly, ultrasonicated in DI water and baked at 160°C in a convection oven for 20 minutes. As-synthesized films were found to have high dielectric constant and loss due to entrapped hydroxyl groups. Hence they were subjected to various post-hydrothermal treatments such as Rapid Thermal Processing and oxygen plasma treatment. These treatments can be expected to remove the hydroxyl groups either by thermal activation or reaction with oxygen ions in the plasma.

The films were characterized using X-ray diffraction, scanning electron microscopy, Raman and FTIR spectroscopy. A Dilor XY 800 Raman microprobe (JY, Inc., Edison, NJ) with an Ar⁺ laser operating at 5145 Å was used to collect the Raman spectra. Low frequency dielectric measurements were carried out using parallel plate capacitor structures. The unreacted titanium served as bottom electrode while the top electrode was copper evaporated through a shadow mask. Capacitance and loss tangent were measured using Agilent LCR meter at 100 kHz. The dielectric constant was calculated using the thickness measured from SEM cross-sections (Fig. 1), which was found to be 300 nm.

2.2. High Frequency Characterization

The dielectric constant of the films from 100 MHz to 8 GHz was estimated using a multiline Coplanar Waveguide method. Coplanar waveguides of different lengths were fabricated on BaTiO₃ films grown by hydrothermal synthesis. The dielectric constant and loss of BaTiO₃ were extracted from s-parameters as described in reference [6]. In this study Coplanar Wave

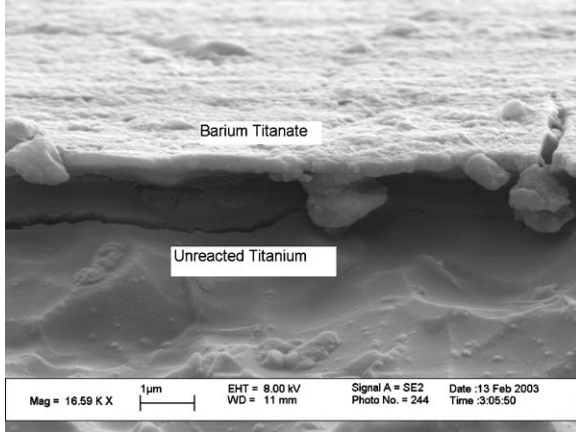


Fig. 1. SEM cross-section of BaTiO₃ film synthesized on 12.5 μm thick Ti foil in 2 M Ba(OH)₂ solution at 95°C.

Guide structures were used. Due to the high dielectric constant of barium titanate films, impedance match between the transmission lines and the Network Analyzer probe tip could not be achieved with processable line widths and spacings. The use of multiline technique eliminates the errors associated with such an impedance mismatch [7].

The propagation factor (γ) of a transmission line structure on a dielectric can be calculated from the s-parameters measured on CPW lines of different lengths.

$$\gamma = \frac{a \cosh\left(\frac{1}{2} \text{Tr}(M_1 M_2^{-1})\right)}{\Delta L} \quad (1)$$

where ΔL is the difference in length of the CPW lines, and M_1 and M_2 are ABCD matrices for different lengths as defined below.

$$A = \frac{(1 + s_{11})(1 - s_{22}) + s_{12}s_{21}}{2s_{21}} \quad (2)$$

$$B = Z_0 \frac{(1 + s_{11})(1 + s_{22}) - s_{12}s_{21}}{2s_{21}} \quad (3)$$

$$C = \frac{1}{Z_0} \frac{(1 - s_{11})(1 - s_{22}) - s_{12}s_{21}}{2s_{21}} \quad (4)$$

$$D = \frac{(1 - s_{11})(1 + s_{22}) + s_{12}s_{21}}{2s_{21}} \quad (5)$$

γ can also be expressed as

$$\gamma = \sqrt{(R + j\omega L)(G + j\omega C)} \quad (6)$$

where R , L , G and C are respectively the resistance, inductance, conductance and capacitance per unit length of the transmission line.

Since dielectric and metallic losses cannot be separated using measurements made on the unknown material alone, identical structures were fabricated on a film (PECVD Silicon Nitride) with same thickness and known dielectric properties. Applying Eq. (6) to Silicon nitride and Barium Titanate,

$$\frac{\gamma_1}{\gamma_2} = \frac{\sqrt{(R_1 + j\omega L_1)(G_1 + j\omega C_1)}}{\sqrt{(R_2 + j\omega L_2)(G_2 + j\omega C_2)}} \quad (7)$$

The CPW structures on silicon nitride and barium titanate were identical. Therefore, the equation reduces to,

$$\frac{\gamma_1}{\gamma_2} = \frac{\sqrt{(G_1 + j\omega C_1)}}{\sqrt{(G_2 + j\omega C_2)}} \quad (8)$$

where G is associated with the loss tangent. C is a function of relative permittivity and geometry of the transmission line structure. G and C can be expressed as [8]

$$C = 2\varepsilon_0(F_{\text{upper}} + \varepsilon_r F_{\text{lower}}) \quad (9)$$

$$G = 2F_{\text{lower}} \omega \varepsilon \tan(\delta) \quad (10)$$

The ratio $F_{\text{upper}}/F_{\text{lower}}$ is a geometrical factor and can be calculated from [9],

$$\varepsilon_{\text{eff}} = \frac{C(\varepsilon_r)}{C(1)} = \frac{(F_{\text{upper}} + \varepsilon_r F_{\text{lower}})}{(F_{\text{upper}} + F_{\text{lower}})} \quad (11)$$

where $C(1)$ and $C(\varepsilon_r)$ are the capacitances when the CPW lines are fully embedded in air and dielectric respectively. Substituting Eqs. (9)–(11) into Eq. (8), the dielectric constant and loss tangent of the barium titanate films can be solved by using the known properties of silicon nitride.

The scattering parameters were measured using an S-parameter Network Analyzer (HP Model 8720 ES). The probes were calibrated using Open, Short and matched 50 Ohm structures on aluminum oxide substrate. The dielectric constant and dielectric loss for the PECVD silicon nitride standard were known to be 8 and 0.003 from previous measurements. The dielectric constant and loss of BaTiO₃ films were estimated from Eqs. (1)–(5) and Eq. (8).

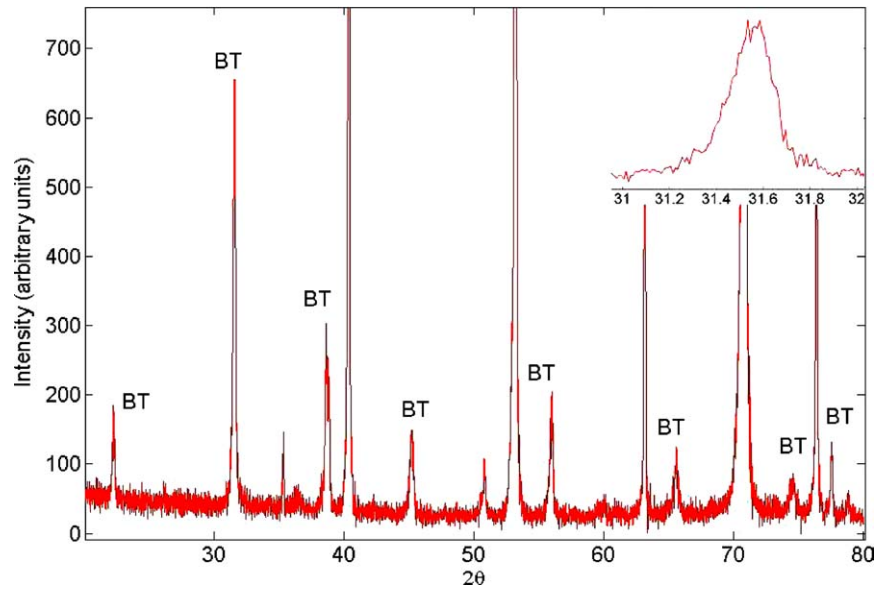


Fig. 2. XRD pattern of barium titanate films synthesized on titanium foil at 95°C with expanded view of the peak at 31.5°.

3. Results and Discussion

The X-ray diffraction pattern of the films synthesized on titanium foil is shown in Fig. 2. Splitting of peaks was not observed and hence it can be inferred that the tetragonal barium titanate, if present, cannot be detected by X-ray diffraction technique. This is expected as the grain size as seen from SEM micrographs (Fig. 3) is around 80 nm. It has been reported that below a

grain size of 80 nm the tetragonality of barium titanate crystals is undetectable by XRD technique. However, regions of tetragonal phases have been reported in hydrothermal nano-crystals [10]. These local tetragonal regions can be detected with Raman spectroscopy as shown in Fig. 4. The Raman spectrum from sintered barium titanate sample is included for comparison. The peaks at 305 and 720 cm^{-1} are specific to tetragonal phase [11].

Low frequency dielectric properties are shown in Table 1. As synthesized films show a high dielectric

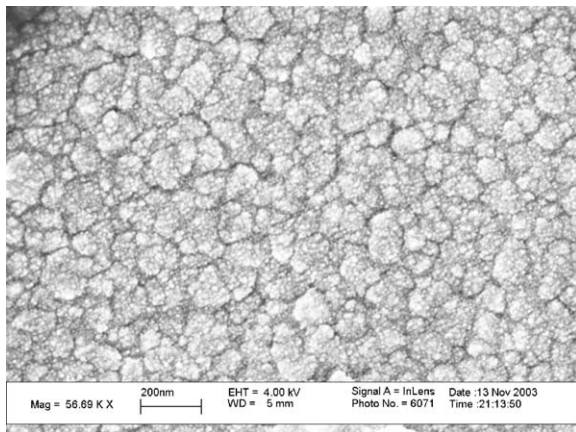


Fig. 3. SEM of surface of BaTiO₃ films synthesized on 12.5 μm thick Ti foil in 2 M Ba(OH)₂ solution at 95°C.

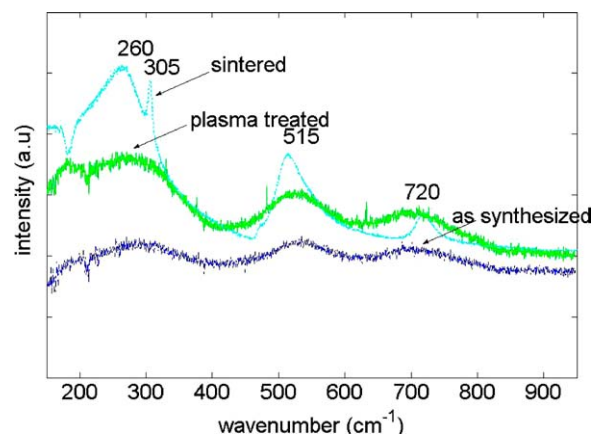


Fig. 4. Raman spectra of hydrothermal films.

Table 1. Dielectric properties of the synthesized films at 100 kHz.

	Specific capacitance (nF/cm ²)	Dielectric constant	Dielectric loss
As synthesized	3000	900	0.28
Plasma treated	1250	370	0.06

constant of about 900 and dielectric loss of 0.28. These dielectric properties are attributed to polarization component from entrapped hydroxyl groups. Annealing in various atmospheres at 300°C has been reported to reduce dielectric loss. In the current study, the lowest dielectric loss achieved by merely heating the film to 300–600°C in conventional oven and in Rapid Thermal Processing chamber using infrared heating lamps was 0.09. Since such high temperature treatments are not compatible with organic boards, oxygen plasma treatment was explored to lower the dielectric loss. Films were subjected to oxygen plasma at a pressure of 200 mTorr and a power of 400 W (12" chamber) for 20 minutes. As can be seen from Table 1, plasma treatment reduces the specific capacitance by half while reducing the loss to 0.06.

The plasma treatment was also found to increase the yield of capacitors while making the films spatially more uniform in terms of dielectric loss. The reactive nature of the oxygen plasma and not the mere heating due to bombardment of the ions in the plasma caused the change in the dielectric loss. This was confirmed from measurements made on samples treated with argon plasma. These samples did not show any change in dielectric loss compared to those without plasma treatment. The effect of plasma treatment on the presence of hydroxyl groups in the films was also studied through Raman and FTIR spectroscopy.

FTIR spectra of the films show the presence of broad peaks corresponding to hydroxyl groups. These are considerably reduced after the plasma treatment (Fig. 5). Hydroxyl groups inside the perovskite lattice can exist in five different lattice sites around the oxygen, and their absorption bands for the stretching vibration appear in the narrow range of 3462.5 to 3509.5 cm⁻¹. Surface hydroxyl groups had very broad bands from 3000–3600 cm⁻¹ because of their absorption on many sites [12]. The FTIR spectrum from plasma-treated samples showed a smaller hydroxyl peak indicating that some of the surface hydroxyl groups were eliminated. Noma et al. also suggest that a Raman peak at 810 cm⁻¹ corresponds to

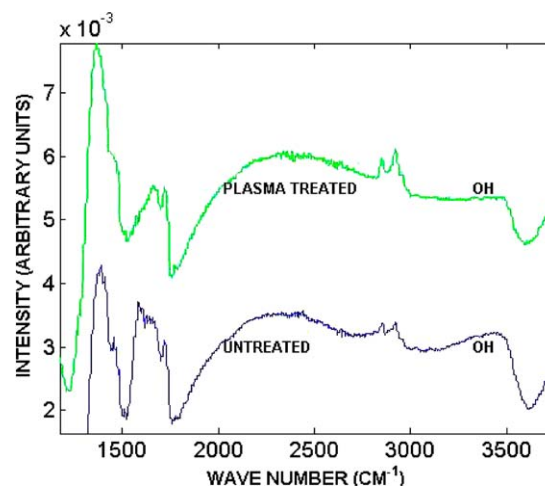


Fig. 5. FTIR spectra of films before and after plasma treatment.

lattice hydroxyl groups. This peak cannot be detected in the Raman spectra (Fig. 4) for the films produced in this study. Hence, the presence of lattice hydroxyl groups and any possible effects of oxygen plasma on their concentration cannot be deduced directly from either FTIR or Raman spectra. However, the Raman peaks at 305⁻¹ and 720 cm⁻¹ are marginally more intense after the plasma treatment suggesting slight increase in tetragonality. Hydrothermal BaTiO₃ crystals are believed to have near cubic structure because of entrapped hydroxyl groups [12]. It is then possible that upon plasma treatment, concentration of lattice hydroxyl groups also decreases resulting in regions of tetragonality in the film which is manifested as more intense peaks in the Raman spectra.

The dielectric constant and dielectric loss characterized from the high frequency s-parameter measurements are shown in Fig. 6. The high frequency dielectric constant was found to be 370, identical to that measured using an LCR meter at 100 kHz, hence suggesting that the dielectric constant is stable from 100 kHz to at least 8 GHz. Previous studies in literature [1] indicate that, with decreasing grain size, the relaxation frequency of BaTiO₃ increases and its dielectric constant decreases. In nano-grained barium titanate ceramics, the individual grains consist of single ferroelectric domain. For a grain size of 100 nm, McNeal et al. [13] used an inverse relationship between relaxation frequency and grain size, and calculated a relaxation frequency of 7.56 GHz. The films in the current study have a grain size close to 80 nm and hence can be expected to exhibit a higher relaxation frequency. This study indicates

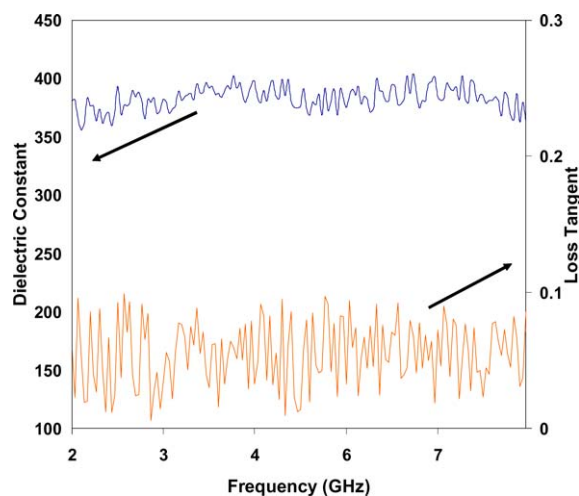


Fig. 6. Dielectric constant and loss obtained from s-parameter measurements.

that thin nano-grained films with relatively high capacitance densities that are stable in GHz frequency range can be obtained using low-cost and low-temperature hydrothermal techniques.

4. Conclusions

Hydrothermal synthesis of barium titanate films is a promising technology for realizing integral capacitors. Nanograined ultrathin crystalline barium titanate thin films were synthesized on laminated titanium foils using this low cost process. The resultant films exhibited a dielectric constant of 350 and loss of 0.06. The films can be integrated on low cost organic boards via standard build-up processes. Thinner titanium foils were found to give better quality films. Oxygen plasma treatment has been shown to reduce the loss of the films for the first time. The high frequency dielectric properties were estimated from s-parameter measurements using

a multiline calibration technique and were found to be stable up to 8 GHz. The films were characterized with Raman and FTIR spectroscopy to study the hydroxyl groups.

Acknowledgments

This work was supported by the National Science Foundation (NSF) through the NSF ERC in Electronic Packaging (EEC-9402723) at Georgia Institute of Technology. Raman spectroscopy work was supported by Division of Materials Sciences and Engineering, U.S. Department of Energy, under Contract DE-AC05-00OR22725 with UT-Battelle, LLC.

References

1. M.P. McNeal, S.J. Jang, and R.E. Newnham, *J. Appl. Phys.*, **83**, 3288 (1998).
2. www.nemi.org.
3. Z. Wu and M. Yoshimura, *Sol. State Ionics*, **122**, 161 (1999).
4. M.A. McCormick and E.B. Slamovich, *J. Am. Ceram. Soc.*, **83**, 442 (2000).
5. M.A. McCormick and E.B. Slamovich, *J. Eur. Ceram. Soc.*, **23**, 2142 (2003).
6. M.Q. Lee and S. Nam, *IEEE Microwave Guided Wave Lett.*, **6**, 168 (1996).
7. D.C. Degroot, D.K. Walker, and R.B. Marks, *Elect. Performance Electron. Packaging*, IEEE 5th Topical Meeting (IEEE publications, Piscataway, N.J., 1996), vol. 28, p. 141.
8. W. Heinrich, *IEEE Trans. Microwave Theory Tech.*, **41**, 45 (1993).
9. G. Ghiione and C.U. Naldi, *IEEE Trans. Microwave Theory Tech.*, **35**, 260 (1987).
10. S.W. Lu, B.I. Lee, Z.L. Wang, and W.D. Samuels, *J. Cryst. Growth*, **219**, 269 (2000).
11. L.H. Robins, D.L. Kaiser, L.D. Rotter, P.K. Schenck, G.T. Stauff, and D. Rytz, *J. Appl. Phys.*, **76**, 7487 (1994).
12. T. Noma, S. Wada, M. Yana, and T. Suzuki, *J. Appl. Phys.*, **80**, 5233 (1996).
13. Mark P. McNeal, Sei-Joo Jang, and Robert E. Newnham, ISAF'96, *Proc. Tenth IEEE Inter. Symp. Appl. Ferroelec.*, **2**, 18 (1996).