

Figure 2. TEM of ceramic body treated at 1450 °C.

formation of crystalline TiB_2 was observed only upon heating of samples for either longer times (1000 °C, 3 days) or at higher temperatures (1200 °C, 1 h). The spectrum shown in the figure obtained from the sample annealed at 1200 °C for 2 h clearly indicates the presence of both crystalline TiB_2 and TiN. The decrease in the linewidths in the spectrum of the 1450 °C sample is consistent with an increase in the average crystal size.¹³ SEM studies of bodies prepared at 800, 1000, 1200, and 1450 °C also indicate a change in morphology after 1000 °C suggesting the onset of reaction.

Consistent with the above results, TEM analysis of the compact annealed at 800 °C for 9.5 h shows the presence of 20–100-nm spherical crystals embedded in an amorphous matrix. These crystals could be either unreacted titanium metal or nucleated titanium nitride. For the ceramic compact annealed at 1200 °C,¹² TEM shows angular grains on the order of 50–100 nm which have two contrast levels. While it is tempting to assign these contrast levels to the two phases detected by X-ray diffraction, electron diffraction was impossible due to the size of the crystals. In agreement with the XRD study, the TEM of the 1450 °C sample presented in Figure 2, shows that two types of grains are still evident but that they have increased in size. There is some indication of a residual amorphous phase in both the images and electron diffraction patterns.

The preparations of TiB_2/TiN and $\text{TiB}_2/\text{Ti}(\text{CN})$ composite materials by sintering TiB_2 and TiN or TiCN powders at high temperatures have previously been reported.¹⁴ Seyferth has also reported that a crystalline TiB_2/TiN powder composite can be made by the pyrolysis of $[\text{B}_{10}\text{H}_{12}\text{-diamine}]_x$ polymer/Ti under NH_3 atmosphere.⁷ TiB_2/TiN composite coatings have also been achieved by CVD methods.¹⁵ The polyborazylene-based route discussed herein is unique, however, in that it is the only reported direct chemical method which can be used to produce monolithic titanium boride/nitride composites, consisting of intimately mixed polycrystals with grain sizes on the order of nanometers, in high ceramic and chemical

yields. The dependence of the crystal size and its distribution on the reaction/sinter temperature, the evolution of microstructure and the properties of the final composite material, such as conductivity and hardness are currently under investigation. We are also exploring the reactions of polyborazylene with other metals and soluble metal complexes with the goal of developing a range of new metal boride/nitride precursor systems that will allow the formation of both shaped bodies and coatings.

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Registry No. Ti, 7440-32-6; TiN, 25583-20-4; TiB_2 , 12045-63-5; polyborazylene, 143186-38-3.

Stable Second-Order Nonlinear Optical Polyimide/Inorganic Composite

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The second-order nonlinear optical (NLO) properties of polymeric materials have been attracting a lot of attention,^{1–15} especially for such potential applications as fast waveguide electrooptic modulation and frequency-doubling devices. The ultimate applicability of polymeric materials for second-order nonlinear optics may depend upon the ability to produce polymers whose orientation has sufficient stability for incorporation into practical devices.⁴ To

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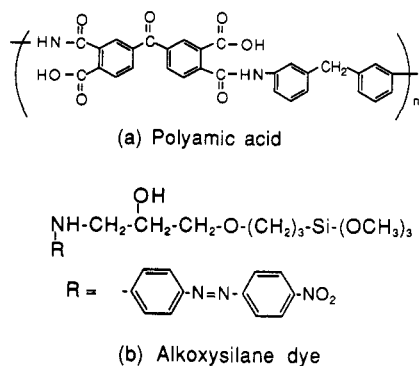


Figure 1. Chemical structures of the aromatic polyamic acid and alkoxy silane dye.

prevent the randomization of the aligned (poled) molecules, NLO chromophores are usually incorporated or covalently bound into either a high T_g polymer or a cross-linked polymer network. Several researchers have reported relatively good high-temperature stability of second-order NLO properties in such types of polymeric materials.^{5,6,8-11}

Aromatic polyimides have been widely used in the electronic industry because of its low dielectric constant, ease of processing, and high-temperature stability.¹⁶ Polyimide films containing a homogeneous dispersion of SiO_2 particles have been achieved by means of a sol-gel process.^{17,18} This sol-gel process involves the sequential hydrolysis and polycondensation of alkoxy silane (namely silicon alkoxide) at temperatures that are commonly used to process polymeric materials.¹⁹⁻²³ Therefore, the sol-gel reaction can take place in the polymer matrix to prepare organic/inorganic composites. This type of composite has the characteristics of high-temperature processing: high modulus and strength even at high temperatures, and a low thermal expansion coefficient. There are other reasons for choosing polyimide as the polymer matrix in this type of organic/inorganic composite. The internal production of water due to the curing of polyamic acid aids the hydrolysis of the alkoxy silane. Moreover, the carboxylic acid group of the polyamic acid, being a Bronsted acid, might have a catalytic effect on hydrolysis and condensation of the alkoxy silane.²⁴

In addition, the high T_g of polyimides would be expected to stabilize the aligned NLO chromophores by decreasing their mobility. Recently, Wu et al. have reported a series of papers where polyimide is used as the host in an organic guest/host system.²⁵⁻²⁸ They demonstrated that the

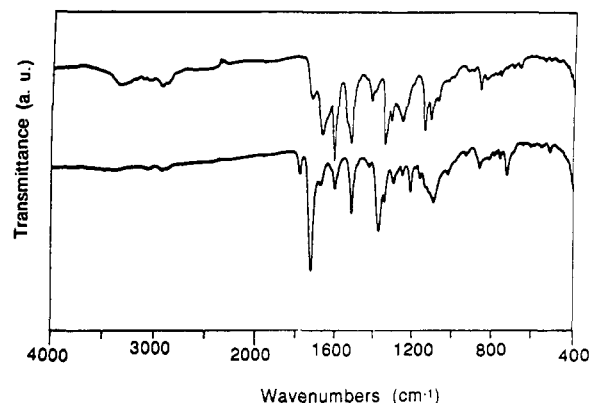


Figure 2. Infrared spectra of the polyamic acid/ASD: (top) pristine; (bottom) cured.

electrooptic (EO) response of the poled organic guest-host material is stable at relatively high temperatures. In one example, the EO response of a poled and cured guest-host polyimide was found to be stable at 150 °C for 12 h.²⁵

In the present study, the first preparation (to our knowledge) of a second-order NLO polyimide/inorganic composite is reported. Alkoxy silane bonded with a NLO chromophore was added to the polyamic acid derived from methylene dianiline and 3,3',4,4'-benzophenonetetracarboxylic acid anhydride. Following thermal curing and poling, transparent polyimide films containing NLO moieties were obtained. The poled film of this polyimide/inorganic composite showed a large second-order NLO effect and excellent temporal stability at 120 °C over 168 h.

The samples for which data are presented use Skybond 705, a polyamic acid (19.5 wt % in 1-methyl-2-pyrrolidinone (NMP)) derived from methylene dianiline and 3,3',4,4'-benzophenonetetracarboxylic acid anhydride, available from Monsanto Chemical Co. The chemical structure is shown in Figure 1.

The alkoxy silane dye (ASD, Figure 1) of (3-glycidopropyl)trimethoxysilane and 4-(4'-nitrophenylazo)phenylamine (disperse orange 3, commercially available) was synthesized according to literature procedures.²⁹ ASD (0.15 g) in 1 g of acetone and 1.5 g of NMP was added to 4 g of a polyamic acid solution. Films were prepared by spin-coating the polyamic acid/ASD solutions onto 1-mm-thick transparent microscope slides (Fisher Premium) and then baked at 70 °C under vacuum for 24 h to remove residual solvent. Typical thicknesses obtained were approximately 0.635 μm for the polyimide/ASD. Indexes of refraction at two different wavelengths (532 and 1064 nm) were measured using an ellipsometer. They are 1.687 and 1.523 for 532- and 1064-nm wavelengths, respectively. The absorption characteristics of the NLO molecules in the polymeric film were recorded on a UV-vis-near-IR spectrophotometer.

The film was poled by the corona discharge method. The details of the corona poling setup have been reported earlier.³⁰ After the sample was poled at 80 °C for 6 min, the temperature was increased to 220 °C to cure the sample. During this period (curing time) the poling field was kept on. The sample was maintained at 220 °C for 4 h and then cooled to room temperature with the poling field on.

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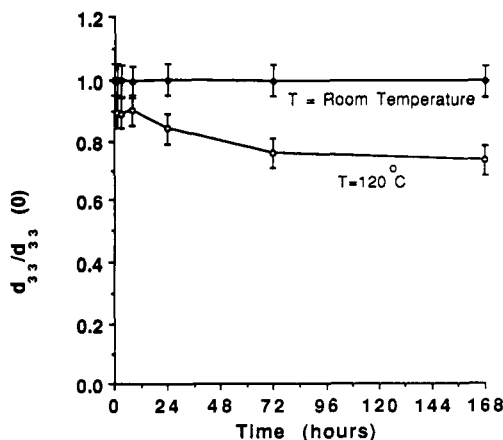


Figure 3. Time behavior of the second harmonic coefficient of poled polyimide/ASD.

The curing temperature was chosen to be 220 °C because the thermal decomposition temperature (T_d) of ASD was determined to be approximately 237 °C (onset point) by a thermogravimetric analyzer at a heating rate of 10 °C/min in air. A period of 4 h was chosen as the curing cycle based on the curing reaction status monitored by FTIR.

The second-order NLO properties of the poled polyimide/ASD samples were measured by second harmonic generation (SH). The polarized Q-switched Nd:YAG laser with 10-ns pulse width and 20-Hz repetition rate was used as the light source. The typical energy per pulse of the laser was 15 mJ. The fundamental laser beam after passing through the sample was blocked by CuSO_4 solution and a 532-nm interference filter. The SH signal was detected by a photomultiplier tube and averaged over 300 pulses in a boxcar integrator. The SH intensity of a Y-cut single crystal of quartz with known thickness and d_{11} value ($d_{11} = 0.364$ pm/V)³¹ was measured as a reference mounted at the same position as that of the sample. The detailed experimental setup and calculations of the second-order NLO coefficient d_{33} have been previously discussed.^{32,33}

IR spectra of the polyamic acid and the cured polyamic acid (polyimide) were taken. The cured sample showed new IR bands at 1778, 1723, and 1375 cm^{-1} . These new bands are attributed to the imide absorption.³⁴ In addition, the absorption change is negligible in the range of 1200–800 cm^{-1} after curing.

After curing of the polyamic acid/ASD at 220 °C for 4 h, an appreciable change of absorbance in the IR spectra was observed due to the emergence of imide absorptions at 1788, 1724, and 1373 cm^{-1} (Figure 2). It is noted that the absorption peak around 1100 cm^{-1} becomes broader and more complex after curing. This suggests that Si–O–Si bonding has formed.^{35,36} The IR data also indicate that the NLO moieties still remained undegraded during the curing process. This is illustrated by the symmetric nitro absorption at 1340 cm^{-1} and the C–N stretching of the aromatic nitro compound at 861 cm^{-1} .^{37,38} These two

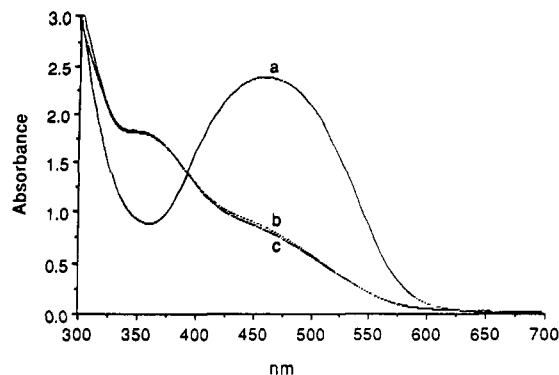


Figure 4. UV-vis absorption spectra of the polyamic acid/ASD: (a) pristine; (b) immediately after poling/curing; (c) poled/cured samples, after thermal treatment at 120 °C for 168 h.

absorption peaks showed negligible change after curing.

The curing behavior of the polyamic acid and polyamic acid/ASD was studied by differential scanning calorimetry (ramp 50 °C/min). The T_g of the cured polyamic acid (polyimide) is 251 °C. However, the T_g of the cured polyamic acid/ASD was not observed up to 275 °C, perhaps due to the suppression of the glass transition by the formation of an inorganic matrix network.

The poled and cured film has a d_{33} value of 13.70 pm/V. The temporal stability at 120 °C of the second-order nonlinearity after poling and curing of the polyamic acid/ASD has been investigated (Figure 3). After over 168 h at 120 °C, a reduction of 27% in d_{33} was observed for the poled polyimide/ASD. Most of this loss was in the first few hours of heating. In addition, the NLO coefficients (d_{33}) of the poled polyimide/ASD remained unchanged under ambient conditions for at least 168 h.

To investigate the absorption behavior as a function of time, the absorption spectrum was taken at regular intervals over a 168-h period for the poled polyimide/ASD kept at 120 °C. An absorption peak at $\lambda_{\text{max}} = 466$ nm existed before poling/curing. Immediately after poling/curing, a large decrease in absorbance at $\lambda_{\text{max}} = 466$ nm was observed (Figure 4). Meanwhile, an absorption peak emerged at $\lambda_{\text{max}} = 345$ nm. As mentioned in the IR study section, the degradation of the NLO dye chromophore is negligible. This implies that the polymer and perhaps the dye moieties possibly undergo a certain extent of conformation change during the curing process. During the next 168 h for the sample held at 120 °C, the absorption spectrum remained almost unchanged. This result suggests that the NLO dye moieties in the composite system did not degrade or sublime throughout the whole period of thermal treatment. Optical quality of the films before and after curing is excellent. This implies that any phase separation must happen at very small scale compared to the light wavelength.

In conclusion, we have shown that an NLO organic/inorganic composite system based on polyimide and alkoxysilane dye has excellent room-temperature stability. After an initial decay, excellent long-term stability at 120 °C is also observed. The stability of the second-order susceptibility achieved in this work is limited by the NLO chromophore degradation temperature. Higher cure temperatures is expected to result in further curing and densification of polyimide and thus enhance the high-temperature second-order NLO stability. An alkoxysilane dye with a NLO chromophore capable of withstanding higher

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cure temperatures provides the possibility for thin films with even more stable second-order nonlinearity.

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Registry No. (BTDA)(DDM) (copolymer), 25038-84-0; (BTDA)(DDM) (polyamic acid SRU), 56802-71-2; (BTDA)(DDM) (polyimide SRU), 26913-87-1.

Low-Temperature Atmospheric Pressure Chemical Vapor Deposition of Titanium Disulfide Films

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Titanium disulfide (TiS_2) has attracted considerable technological attention, due to its favorable attributes as a cathode material in lithium batteries^{2,3} and, to a lesser extent, for its application as a component in lubricating coatings for titanium alloys.⁴ Recent emphasis on the development of thin-film lithium batteries has underscored the need for high-purity, crystallographically oriented, stoichiometric coatings.³ TiS_2 films have been largely prepared by chemical vapor deposition (CVD) routes involving titanium tetrachloride and hydrogen sulfide,³ although radio frequency (rf) sputtering⁵ and sulfurization of titanium metal⁶ have been demonstrated to provide coatings. All of these strategies possess inherent limitations, including a wide range of titanium to sulfur stoichiometries, high deposition temperatures (400–800 °C), and concomitant substrate restrictions. Since lithium battery performance has been shown to be critically de-

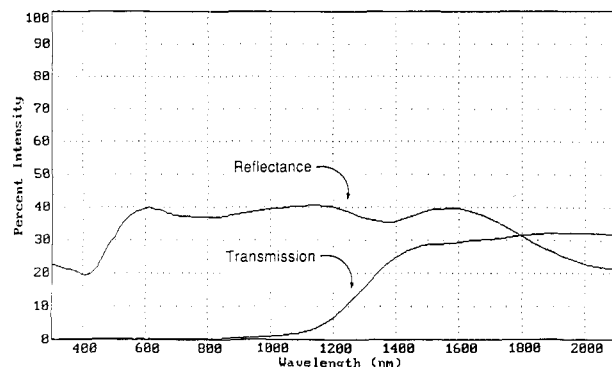


Figure 1. Reflectance/transmission spectra of a film prepared at 500 °C.

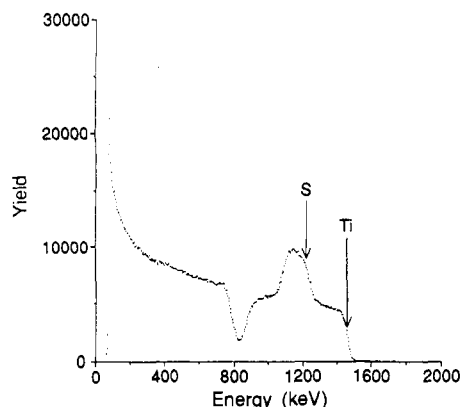


Figure 2. Rutherford backscattering spectrum of a film prepared at 300 °C.

pendent upon the crystallographic orientation of the TiS_2 cathode film,^{3a,b} any process that will be of use in battery applications must provide a suitable orientation. Herein we report a new atmospheric pressure CVD process for titanium disulfide films which relies upon the reaction of titanium tetrachloride with organothiols at temperatures as low as 200 °C.⁷ This procedure affords stoichiometric TiS_2 coatings with crystallographic orientations that are optimum for use in lithium batteries. The facility of the film formation indicates that a remarkably efficient carbon-sulfur bond cleavage is operant. Importantly, the low-temperature nature of this process should greatly expand the range of substrates upon which TiS_2 films can be deposited.

Adhesive, highly reflective gold-colored films of TiS_2 could be deposited on glass, silicon, and stainless steel substrates in the temperature range 200–600 °C using the atmospheric pressure CVD reaction of titanium tetrachloride and *tert*-butylthiol in a horizontal hot-walled reactor. Deposition rates for films grown at 400 and 600 °C under these conditions were 247 and 280 Å s⁻¹, respectively.⁸ Other organothiols (e.g., ethanethiol, 2-butanethiol, 1-propanethiol) were equally effective at providing films between 200 and 600 °C, but their volatilities were either too high or too low for convenient use. Dimethyl sulfide and dimethyl disulfide both failed to afford films with titanium tetrachloride in the temperature range 200–600 °C.⁹

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