Articles

Laser-Induced Conversion of Molecular Precursors to Thin Films and Deposited Layers

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A study has been conducted on silicon nitride deposits formed by dissociation of liquid-phase molecular precursors that were introduced directly into a laser–substrate interaction zone. An important feature of these new precursors, e.g., a silazane monomer (mol wt 220–320), is a high conversion yield from liquid to solid. Another feature is the strong absorption of 10.6-μm wavelength radiation. With use of newly designed precursors, several compounds including silicon nitride, have been formed on solid substrates and supporting grids by CO_2 laser pyrolysis. Film thicknesses range from 500 Å to many microns, with growth rates as high as several microns per second. To accomplish this, a nitrogen jet is used to continuously spread the liquid precursors as a thin layer in the beam–substrate (or grid) interaction zone. In this process the precursor's viscosity and evaporation rate are critical factors. These, together with the nature of the molecule–photon interaction and associated chemical reactions, are all factors in developing new molecular precursors.

Introduction

A wide range of surface coating materials can be deposited by chemical vapor deposition (CVD). These deposits have found industrial applications for semiconductor devices, wear resistance, corrosion protection, and optical fibers. In a conventional CVD reaction the substrates are placed in a furnace, and reactive gases are passed over them. The high temperature breaks the molecular bonds, and the resulting products recombine to form the desired coatings on the substrate. Though effective and reliable, CVD processing is slow, is wasteful of expensive and hazardous reactants, and is limited to materials that can withstand the high temperatures involved.

The scope of the CVD method is extended by using laser radiation since it is possible to exploit a diversity of pyrolytic and photolytic reactions.[1-3] In these reactions the laser radiation may excite (i) the gas-phase molecules, (ii) the adsorbed chemical species on the surface, or (iii) the substrate atoms. Compared with other radiant energy sources the laser has the advantages of facilitating localized reactions and of selective coupling with specific materials. Furthermore, the high-energy density promotes rapid synthesis of deposit material with minimal contamination.

An appropriate precursor for laser CVD must possess the following features: (i) strong absorption of 10.6-μm wavelength radiation; (ii) high liquid-to-solid conversion yield; (iii) low toxicity. When a liquid molecular precursor is introduced directly into the laser–material interaction zone (Figure 1), the desired properties include a low volatility and a moderate viscosity. It should be noted that while molecular carbon-containing precursors have attractive features, they also have a tendency to introduce carbon into the deposit.[6,7] While a previous study suggests that the deposition is the result of the direct laser decomposition of the liquid into a solid, an additional mechanism has now been observed.[4]

As shown in Figure 1, rapid heating of the liquid precursor chemical creates aerosol droplets through solvent boiling and evaporation. These droplets continue to react with the beam to form a range of deposits when they return to the surface.[5] The largest will remain liquid and leave a dry precipitate when the solvent is fully vaporized. The evaporation cools the substrate and roughens the deposit. Slightly smaller drops will form dry solids that create clusters and fall on the surface. Further heating of these clusters may cause them to vaporize. Finally, as shown in the right-hand side of Figure 1, even smaller liquid droplets are converted into solid particles that are sufficiently small to be completely vaporized. Subsequent condensation from this vapor produces CVD type surface deposits.

Experimental Section

Precursor Synthesis and Properties. The precursors prepared for laser-induced conversion to silicon nitride are based on previously synthesized compounds.[8] Experimentally they were synthesized by the ammonolysis of methyl dichlorosilane, CH_3SiHCl_2, in a process involving cannulation of diethyl ether and methyl dichlorosilane into a flask cooled to 0 °C in an ice bath.

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(1) Cannon, W. R.; Danforth, S. C.; Haggerty, J. S.; Marra, R. A. *J. Am. Ceram. Soc.* **1982**, *65*, 330.
(2) Flint, J. H.; Haggerty, J. S. *Proc. SPIE–Int. Soc. Opt. Eng.* **1984**, *458*, 108.
(3) Froidevaux, Y. R.; Gllgen, H. H. *Appl. Phys. A* **1985**, *37*, 121.
(4) Partridge, J. P. Surface Synthesis via Lased-induced Reactions. *Mater. Res. Soc. Proc.* **1988**, *101*, 443.
(5) Siefert, W. *Thin Solid Films* **1984**, *121*, 275.
(6) Beatty, C. L. In *Ultrastructure Processing of Advanced Structural and Electronic Materials*; Hench, L. L., Ed.; Noyes Data: Park Ridge, NJ, 1984; p 256.
(7) Allen, S. D. *Proc. SPIE–Int. Soc. Opt. Eng.* **1979**, *198*, 49.
(8) Afanasev, V.; Krokhin, O. N. *Soviet Phys. JETP* **1967**, *25*, 639.

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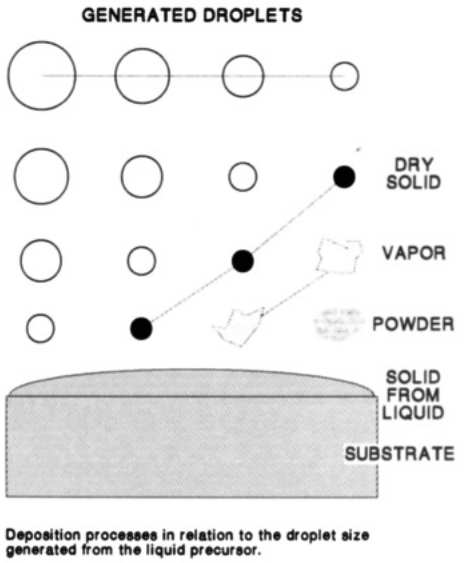

Figure 1. Effect of precursor droplet size in determining the specific deposition mechanism.

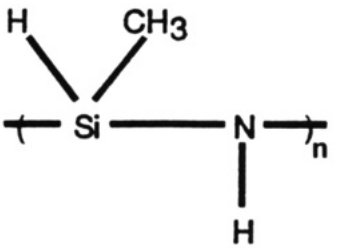

Figure 2. Molecular structure of silazane monomer.

An excess of anhydrous ammonia was bubbled into the flask with vigorous stirring until the solution was strongly basic. The reaction mixture was stirred for another 2 h and then filtered under argon. The solvent was removed via trap-to-trap distillation under vacuum, leaving an oily residue. The ammonolysis product consists mainly of cyclics $(CH_3SiHNH)_x$ with $x = 3$ and 4 (Figure 2), the major component being the $x = 4$ cyclic. The molecular weight is about 290 g/mol. In addition to the silazane monomer, a polymerized liquid with a molecular weight of about 1000 was also synthesized.

Optical measurements were obtained to determine the energy coupling characteristics of the monomer with CO_2 laser radiation. Fourier transform infrared spectroscopy revealed a strong absorption peak in the 10.6-μm wavelength region. From absorption measurements on samples of varying solvent dilution, Beer's law was shown to be obeyed, i.e., $I = I_0 \exp(-\alpha X)$. The term α is the absorption coefficient, and X is the liquid depth. Experimentally, the value of α at a wavenumber of 941 cm^{-1} (or 10.6 μm) was 45.196 cm^{-1}. This shows that 95% of the radiation is absorbed within a depth of 11 μm.

Processing Procedure. In the experimental arrangement used to synthesize silicon nitride deposits (Figure 3), a Control Laser Model IL-1500 laser irradiated the substrate with 10.6-μm wavelength photons for a preselected time (typically 2–10 s). All experiments were conducted using a beam power of 700 W. With the beam focused to a 5.5-mm spot diameter, the incident power density was 3000 W cm^{-2}. The arrangement in Figure 3 was used to form (i) thin-film deposits on an electron microscope grid and (ii) thicker deposits on silica and metallic substrates. Prior to each experiment a 0.05-mL volume of precursor liquid was placed on the substrate by using a syringe. In some experiments this liquid was spread over the substrate by a jet of pure nitrogen to produce a thin layer. The liquid was delivered through a 6.5-mm-diameter tube, with a flow-rate in the range 1000–3000 sccm.

In the initial experiments both the monomer and polymer precursors with molecular weights of 300 and 1000, respectively, were used. As a result of the different beam energy coupling with the various substrate materials, the beam duration (interaction time) was varied to obtain optimal results. Specific values used to produce well-formed silicon nitride deposits on silica, nickel, and titanium were 2, 10, and 6 s, respectively. Preparation of grid-supported samples for transmission electron microscopy involved the use of a helium–neon sighting laser. The low-power laser was passed through the grid, and the diffraction pattern noted. The deposition process was begun by injecting the liquid on the grid and applying the high power laser. When the diffraction pattern was partially restored, the process was halted. This procedure provided the ability to reliably produce thin films for TEM studies.

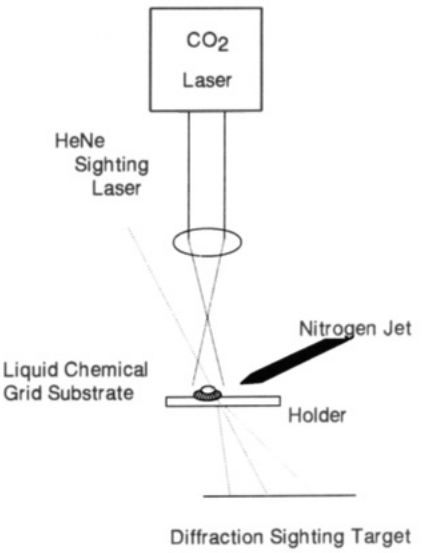

Figure 3. Schematic diagram of arrangement used for laser synthesis of deposited layers.

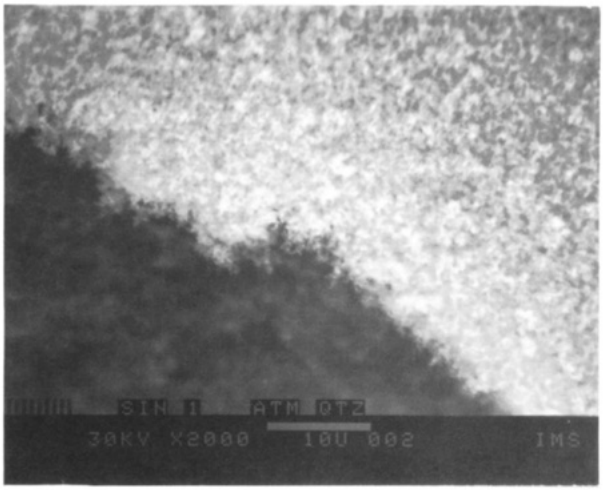

Figure 4. Structureless-type deposit, with a high density of silicon nitride particles that have settled on the surface.

Processing and Structural Features. Substrate-supported silicon nitride films were produced (i) with and (ii) without the nitrogen gas jet. When the jet was employed, the gas stream spread the droplet of precursor liquid over the substrate surface to produce a thin layer. During laser irradiation, a fairly intense white plume formed, and the liquid underwent conversion into a solid layer, of 4–13 μm thickness. X-ray and channeling SEM patterns revealed that this layer was entirely amorphous. The scanning electron microscope also showed that the layer was completely featureless apart from residual powder particles that settled on the surface (see Figures 4 and 5). The fine particles are presumably formed by condensation from the laser plume. When processing did not involve the nitrogen jet, the formation of a yellow plume was preceded by the evolution of white smoke. The interaction with the precursor droplet produced a white powdery deposit. Further irradiation for 10 s resulted in the conversion of this deposit into a strongly adherent surface coating.

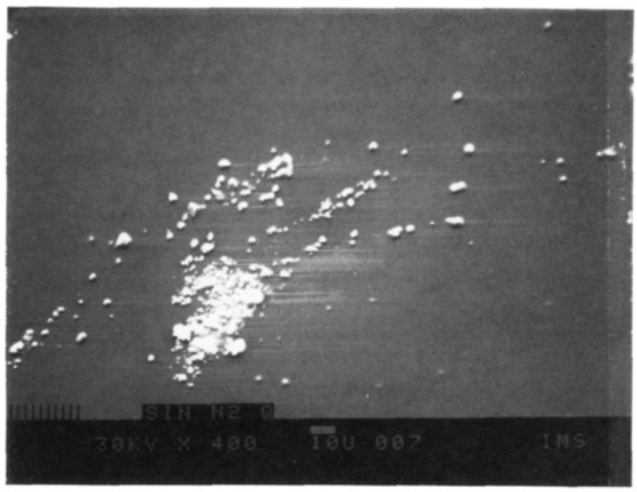

Figure 5. Structureless-type deposit, with a low density of settled silicon nitride particles.

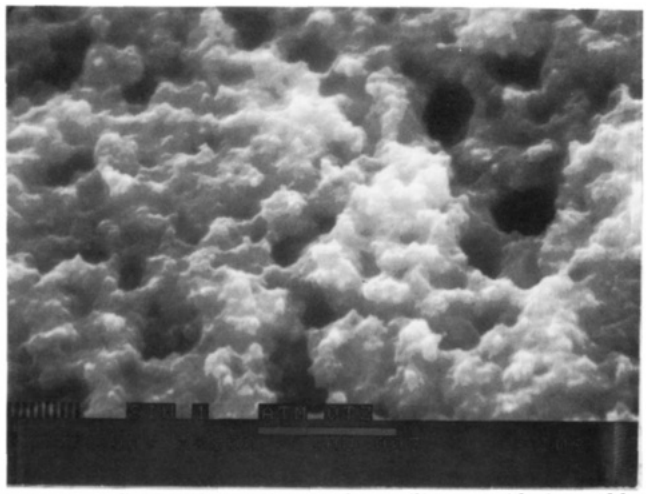

Figure 6. Surface layer of amorphous silicon nitride formed by laser sintering of deposited particles.

Careful examination of Figure 6 clearly reveals the formation of a botryoidal structure by the sintering of small particles. Thus in this case, a high density of particles is formed by rapid condensation of species emerging from the laser plume.[8-12] As revealed by profilometry measurements, the deposits formed by the sintering of these particles had thicknesses ranging from 4 to 20 μm. Analysis of the structures shown in Figure 6, reveals them to be amorphous. The bonding structure in these deposits was characterized by Fourier transform infrared spectroscopy.[13-22] For the sintered particle structure (Figure 6), the FTIR studies revealed a spectrum containing several peaks present in the precursor liquid. This suggests that the deposited layer is essentially a three-dimensional polymer, chemically similar to the original precursor.

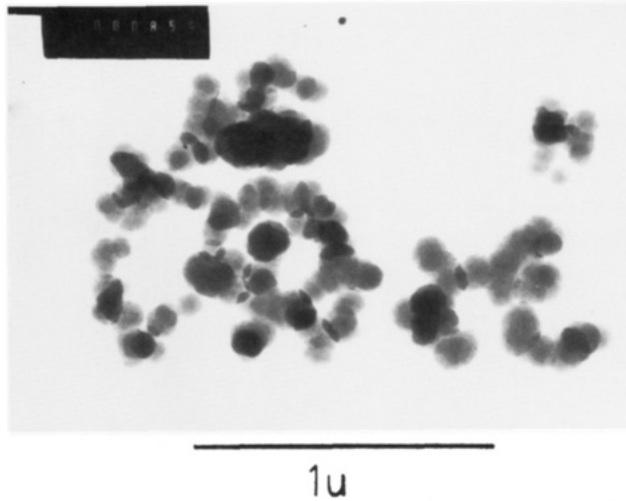

Figure 7. Silicon nitride particles entrapped within a structureless type thin film.

Figure 8. Cracks in structureless-type deposit formed an cooling during postthermal treatment.

Initial attempts to deposit the films directly onto TEM 3-mm grids were unsuccessful. The intensity of the beam was disproportionately absorbed by the thin grating, resulting in severe damage. By using shorter interaction times and by sandwiching several grids in a stack, it was possible to recover films deposited on the lower grids. Examination of the films at high magnification (×140000) revealed an essentially featureless structure. However, they did contain entrapped particles that have formed into chainlike structures (Figure 7). Presumably these particles condense from the laser plume and as such are similar to those forming the botryoidal structure in Figure 6. It may thus be inferred that they are amorphous silicon nitride.

Posttthermal Treatment. Posttthermal treatment studies of the deposited layers at temperatures up to 725 °C showed that the sintered silicon nitride deposits did not undergo detectable change. Furthermore they did not exhibit cracking on delamination. In contrast, the featureless structure deposits delaminated upon cooling and displayed significant surface cracking. An example of deep cracks formed in a deposit, after such treatment, is seen in the scanning electron micrograph in Figure 8. An incident feature in this figure is the high density of fine particles that settled on the surface in the synthesis process.

Discussion and Analysis

Clearly, this preliminary study shows that strong, highly adherent surface deposits are rapidly formed by a process involving (i) generation of an aerosol from a laser-pyrolyzed precursor liquid; (ii) aerosol droplet (or condensed particle)

(9) Knight, C. *AIAA J.* **1979**, *17*, 519.
(10) Ong, C. K.; Tan, H. S.; Sin, E. H. *Mater. Sci. Eng.* **1986**, 79.
(11) Yokoyama, H.; Uesugi, F.; Kishida, S.; Washio, K. *Appl. Phys. A* **1985**, *37*, 25.
(12) Harrach, R. J. *J. Appl. Phys.* **1977**, *48*, 2370.
(13) Seyferth, D.; Wiseman, G. H.; Prud'homme, C. *J. Am. Ceram. Soc.* **1983**, *66*, C13.
(14) Nishino, S.; Honda, H.; Matsunami, H. *Jpn. J. Appl. Phys.* **1986**, *25*, L87.
(15) Gebhardt, J. J.; Tanzilli, R. A.; Harris, T. A. *J. Electrochem. Soc.* **1976**, *123*, 1578.
(16) Peercy, P. S.; Stein, H. S.; Doyle, B. L.; Wells, V. A. *Int. Conf. CVD, 7th* Los Angeles, CA, Oct 14–19, 1979.
(17) Wong, J.; Angell, C. A. *Glass Structure by Spectroscopy*; Marcel Dekker: New York, 1976; p 547.
(18) Rand, M. J.; Roberts, J. F. *J. Electrochem. Soc.* **1973**, *120*, 446.
(19) Gorowitz, B.; Gorozyca, I. B.; Saia, R. J. *Solid State Technol.* **1975**, 197.
(20) Chow, R.; Lanford, W. A.; Ke-Wing, W.; Rosler, R. S. *J. Appl. Phys.* **1982**, *53*, 5630.
(21) Lanford, W. J.; Rand, M. J. *J. Appl. Phys.* **1978**, *49*, 2473.
(22) Arkles, B. *J. Electrochem. Soc.* **1986**, *133*, 233.

transport to the substrate; (iii) particle–particle and particle–substrate sintering.

In considering some of the basic mechanisms involved it should be noted that the generated aerosol faces competing processes of evaporation, coagulation and particle settling. The addition of turbulent fluid flow, chaotic aerosol generation, and laser interaction with reactant chemicals makes the prediction of particle deposition intractable. However, the evaporation lifetime of an aerosol particle can be expressed by

$$t = \frac{R\rho d^2}{8DM(P_p/T_p - P/T)}$$

where R is the gas constant, ρ is the particle density, d is the particle diameter, D is the vapor diffusion coefficient, M is the molecular weight, P_p is the partial pressure at the drop, P is pressure at infinite distance, T_p is the temperature at the drop, and T is temperature at infinite distance. Therefore, the lifetime is proportional to the square of the diameter. For particles of similar size the coagulation will obey the Brownian equation

$$N(t) = \frac{N_0}{1 + N_0kt}$$

where $N(t)$ is the number of particles at time t, N_0 is the initial number of particles, and k is the coagulation coefficient. Through this process the number of particles will decrease as the reciprocal of time. The deposition rate from the aerosol on a surface is given by

$$n(t) = 2n_0(Dt/\pi)^{1/2}$$

where $n(t)$ is the number of particles per unit surface area at time t, n_0 is the initial number available, and D is the diffusion coefficient given by

$$D = \frac{\kappa TC}{3\pi\eta d}$$

where T is temperature, C is the slip correction factor, d is the diameter, η is the viscosity, and κ is Boltzmann's constant. The slip correction factor is given by

$$C = 1 + \lambda/d(2.514 + 0.8\exp(-0.55d/\lambda))$$

where λ is the mean free path of the gas. This leads to the conclusion that the deposition rate depends upon the square root of time and the temperature/viscosity ratio. Future work will investigate the validity of this prediction.

Conclusion

It has been demonstrated that laser synthesis can be used to form amorphous silicon nitride coatings on nickel, titanium, copper, and silica substrates. The method involves the pyrolysis of a molecular precursor to form aerosol droplets that condense into 85–500-mm silicon nitride particles. Following arrival at the substrate, these particles undergo laser-induced sintering, thereby producing a strong, highly adherent surface coating.

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Registry No. Ni, 7440-02-0; Ti, 7440-32-6; Cu, 7440-50-8; SiO_2, 7631-86-9; silicon nitride, 12033-89-5.

Synthesis of Thin Films by Atmospheric Pressure Chemical Vapor Deposition Using Amido and Imido Titanium(IV) Compounds as Precursors

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In an attempt to prepare TiN, the amido- and imidotitanium(IV) complexes $Ti(NR_2)_4$ (R = Me or Et), $Ti(NMe_2)_3(t\text{-Bu})$, and $[Ti(\mu\text{-N-}t\text{-Bu})(NMe_2)_2]_2$ were used as precursors in an atmospheric pressure chemical vapor deposition process. Depositions on glass, silicon, vitreous carbon, and boron substrates were successfully carried out at temperatures below 450 °C to give coatings up to 6000 Å thick and growth rates from 50 to 1000 Å/min. The films, which were characterized by electron microprobe and Rutherford backscattering, contained titanium and nitrogen in a ratio close to 1, plus significant amounts of carbon and oxygen. X-ray photoelectron analyses with depth profiling confirmed that the films are uniform in composition, the nitrogen is Ti bound, and the carbon is both Ti bound and organic. The analyses indicate precursor decomposition mechanisms involving both $Ti-NR_2$ homolytic bond cleavage and amido ligand β-hydride activation, the latter accounting for the presence of Ti-bound carbon in the films. In support of this hypothesis, films made from precursors with cyclic amido ligands, for which β-hydride activation is disfavored, contained only organic carbon.

Introduction

Titanium nitride, TiN, displays an interesting combination of properties.[1] For instance, the optical properties of TiN resemble those of gold, yet it is harder than all elemental metals and sapphire (Al_2O_3) and almost as hard as diamond. Its melting point is almost 3000 °C, which is higher than that of most materials, and it is inert to most chemicals and solvents except aqua regia, which dissolves it slowly, and HF. Titanium nitride is a better electrical conductor than titanium metal.

(1) Refractory Materials; Margrave, J. L., Ed.; Academic Press: New York, 1971.

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