causes for the increase of the solubility limit of NiO as compared with that of MgO.

The temperature dependence of the solubility limit of NiO in Al₂O₃ is also determined using the two values obtained in this work:

 $\ln X = -2.79 - 1.24 \times 10^4 / T$

where X represents the solubility limit of the cationic fraction of Ni/Al and T is the absolute temperature.

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Photolithographic Patterning of Particulate Films

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A method has been developed to produce an arbitrary pattern with a minimum feature size of 5 μ m in a thin particle film on a substrate. In this method, a layer of photoresist is spun onto a continuous, uniform ceramic film which is then exposed to ultraviolet light under a mask with the desired pattern. After development of the photoresist the regions of the film no longer covered with photoresist are removed by immersion in an ultrasonic bath. The vacant regions in this first layer can then be filled with a second material, and multiple layers can be built up by slight modifications to this procedure.

THE formation of fine-scale structures (lines, holes, ditches, etc.) in particulate films offers many opportunities for studying structure/property relationships and kinetic processes, and for forming unique devices and components. In particular, we have considered applications such as sensors; opto-electronics; magnetic data storage; selected area thermal-, chemical-, or wear-resistant coatings; electromagnetic switches; minicapacitors; and, finally, semiconductor packaging. The purpose of this paper is to demonstrate the concepts for forming arbitrary structures in particulate films in a range of dimensional sizes down to 5 μ m. The ability to do this with various materials in single or multiple layers and

the ability to control the microstructure during subsequent interparticle neck growth and densification allow for many new opportunities, especially for ceramics and ceramic-metal mixtures. In earlier papers,^{1,2} the photopolymerization of tapecast sheets and the patterning of thick films using a photolithographic process were discussed. The minimum feature size on these sheets, however, was much larger than 5 μm.

As the miniaturization trend in microelectronics continues, auxilliary components must also be miniaturized to keep pace with advances in integrated circuits. One such auxilliary component is the multilayer ceramic substrate used for integrated circuit packaging. These devices are presently fabricated by first tapecasting ceramic green sheets containing binders, mechanically punching holes in these sheets, screening on refractory metal lines and vias, laminating the sheets together, burning out the binders, and, finally, sintering.

There are various limitations inherent to this process. The variation in lateral shrinkage during sintering introduces a relatively large uncertainty to the relative

planar location of I/O terminals. This may lead to problems when the chips are attached to the substrate, especially as the density of interconnects increases and their size decreases. Other limitations are that the density of I/O terminals is limited by the minimum size hole that can be punched in the sheets and the minimum metal line width that can be produced by screening. Also, the large amount of binder which must be present in the green sheets in order to give them the necessary green strength causes difficulties during cofiring with oxygen-sensitive metals such as copper.

This paper describes a new method for fabricating a device, such as a multilayer ceramic substrate, where continuous regions of one material are isolated from each other by a second matrix material in a layered structure. In this method, a substrate provides physical support for particle layers so that little or no binder need be present. The presence of the substrate also solves the planar location problem since the substrate constrains the film to shrink only in the direction perpendicular to the substrate's surface.

Because it is desirable to produce features smaller than can be produced by screening, and because the presence of the substrate makes mechanically punching holes in the ceramic film impossible, a new process for making patterns in green particle films has been developed. In this process, photolithographic techniques are used to cover certain regions of a ceramic particle layer with photoresist, and a pattern is then formed in the ceramic layer by using sonication to remove those regions of the layer not covered with photoresist. Lines 5 μ m wide and square holes 5 μ m on a side have been made in layers 3 μ m thick using this procedure. Furthermore, using a similar process these holes have been subsequently filled with particles, simulating the filling of via holes with metal in a ceramic package.

EXPERIMENTAL PROCEDURE

Silica powder synthesized by the

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Fig. 1. Basic photolithographic patterning process: (a) photoresist film spun onto particle film on substrate, (b) photoresist exposed to UV light under mask, (c) photoresist developed, (d) sonication to remove portions of particle film, and (e) photoresist removed.

Particle Film

Substrate

Photoresis

Stöber method was used in this work.⁶ In this method, tetraethyl orthosilicate (TEOS) undergoes hydrolysis and condensation reactions in an ammonium hydroxide and ethanol solution to form spherical, submicrometer, monosize silica particles. Silica particles $0.5 \ \mu\text{m}$ in diameter were prepared using 0.3M TEOS, 1.95M NH₃, and 4.0M H₂O in ethanol. The TEOS was distilled prior to use. After synthesis, the suspension was dried by removing the ethanol under vacuum at room temperature. The powder was then redispersed in deionized water or ethanol using an ultrasonic probe.

A suspension containing 15 wt% of the synthesized SiO_2 powder was used to produce a uniform, defect-free, continuous silica film several micrometers thick on either a glass or silicon-wafer substrate. Three different suspension systems were used: heptane, deionized water, and ethanol. In heptane, the silica was dispersed using a nonaqueous dispersant.[†] A concentration of 2 wt% of the nonaqueous dispersant, based on the weight of the silica, was used.

In order to prepare the heptane suspension, heptane containing the desired amount of the nonaqueous dispersant was added to approximately half as much of a concentrated ethanol suspension, and the mixture was subsequently boiled. Boiling increased the heptane concentration since



Fig. 2. Techniques used to fabricate multilayered structures with positive- and negative-image masks: (a) patterned first layer strengthened with polymer, (b) second particle layer cast, (c) photoresist applied, (d_1) and (d_2) resist exposed to UV light under mask, (e_1) and (e_2) resist developed, (f_1) portions of second particle layer strengthened (positive-image mask), (f_2) sonication to remove uncovered portions of second layer (negative-image mask), (g_1) and (g_2) photoresist removed, and (h_1) sonication to remove non-strengthened portions of second layer (positive-image mask).

the vapor was richer in ethanol than the liquid, because the low-boiling azeotrope has a composition of 48% ethanol and 52% heptane. Additional heptane was added as needed until the boiling point of the liquid was equal to that of pure heptane. This allowed production of more uniform films. In the water-based system, 0.1 wt% of the nonionic surfactant polyethylene glycol monolaurate[‡] was added to decrease the surface tension of the suspension. A small amount of ammonium hydroxide was added to some of the ethanol suspensions.

All work to fabricate the green films was done in a class 100 laminar flow hood to minimize dust contamination. Substrates were cleaned prior to film deposition by washing with deionized water, wiping dry with lint-free lens paper, rinsing with a stream of deionized water, and, finally, blow drying with an aerosol duster. About 25 μ L of the suspension was spread into a thin film on the surface of a 2.5 by 7.6 cm substrate using a 0.64 cm diameter glass rod. The rod was situated with its axis parallel to the substrate and perpendicular to

the long direction of the substrate. It was supported about 0.10 mm above the substrate surface. The suspension was dropped near the center of the rod; it spread along the rod by capillary action. The rod was then slid (without rotating) across the substrate, leaving a film of suspension. The films were dried at ambient conditions in the laminar flow hood. Drying was complete in several seconds.

Patterned films were produced using the following procedure,⁷ which is illustrated in Fig. 1. A continuous film of positive photoresist[§] was spun onto the top surface of the particle film at 5000 rpm for 30 s. After prebaking at 90°C for 25 min to harden the photoresist, the sample was placed under a mask in a mask aligner and exposed to ultraviolet light. The exposure time was 5 s at a power of 10.3 mW/cm^2 and a wavelength of 365 nm. The photoresist was then developed by immersing the sample for 60 s in a mixture of equal parts developer' and deionized water. The sample was then rinsed for 30 s with deionized water. This process left the silica layer



Fig. 3. SEM of the top surface of a silica film 3 μ m thick cast from a water suspension (bar=10 μ m).



Fig. 4. SEM of a patterned silica film at high magnification showing 5- μ m lines with 5- μ m spacings (bar=10 μ m).

covered with photoresist only on regions which were under the opaque portions of the mask.

To remove the portions of the particle film no longer covered by photoresist, the sample was placed in a beaker filled with either de-aired, deionized water (for ethanol- or water-based systems) or hexane (for the heptane-based system) and then sonicated for several seconds in an ultrasonic bath.** The remaining photoresist was then removed by dissolution in acetone, leaving a silica film with the desired pattern.

In order to fill the vacant areas in the first layer with a second material, the following procedure (diagramed in Fig. 2) was used. For simplicity, silica was also used in this procedure, although the method is applicable to other materials with similar particle size distributions and dispersibility. The layer patterned as described above was strengthened so that during the subsequent sonication step it would not be removed.

Strengthening was accomplished by applying enough of a solution of mediummolecular-weight poly(methyl methacrylate) (PMMA)^{\dagger †} in acetone (1 g/100 mL) to the first layer so that the weight of the incorporated PMMA was about 1.5% that of the silica in the layer. The PMMA solution was applied with a glass rod. A second layer of silica was then applied on top of the first, using an ethanol suspension and the method described earlier. Photoresist was applied and processed as above, except that the mask had to be aligned over the pattern in the first silica layer using a mask aligner (either the same mask used in the first step or one with its negative image was used). The photoresist was then developed. (Only the case of positive photoresist will be discussed, although negative photoresist has also been used.)

If the negative-image mask was used, the sample was next sonicated in hexane (since water damages the PMMAstrengthened first layer) to remove those portions of the second silica layer no longer covered by the photoresist. The remaining photoresist was then removed using acetone or methanol if the PMMA from the first layer was not to be removed.

When the same mask used in the first step is used in the second step, a compatible system of binder, photoresist, and solvents is important. This is due to portions of the second silica layer filling the vacant areas in the first layer not being covered with photoresist after development, because the exposed photoresist dissolves away during this step. Therefore, these regions must be strengthened with PMMA in xylene (1 g/100 mL) to prevent their removal during subsequent sonication. Xylene was used as the solvent instead of acetone because acetone would dissolve the remaining photoresist over the patterned first layer. This is important, as this photoresist must serve as a barrier during PMMA application to prevent the PMMA solution from penetrating the regions of the second silica layer and strengthening them. If those regions were also strengthened, this unwanted silica could not be removed during sonication, resulting in a continuous, unpatterned film.

After the PMMA application, however, the remaining photoresist must be removed to allow sonication of the unwanted silica. This leads to another complication inherent to this particular method: during the strengthening of the second silica layer, the remaining photoresist is covered with a very thin coating of binder. This makes removal of the photoresist difficult, because the solvent used must not dissolve the PMMA that is strengthening the silica layer. To get around this, the sample was soaked in methanol for 15 min, because this solvent removes the photoresist but does not affect PMMA. After these preliminary steps, the sample was finally sonicated in hexane to remove the unstrengthened portions of the second silica layer.

RESULTS AND DISCUSSION

Upon drying, the films produced from water suspensions and from ethanol with ammonia suspensions appeared opalescent, indicating ordered packing of the particles in the film. Scanning electron micrographs (SEMs) confirmed this, as shown in Fig. 3. The size of the ordered regions or "grains" varied for each batch of silica from up to 15 μ m across in some films to no larger than 3 μ m across in others. Examination of film fracture surfaces and "vacancies" in the top surfaces of films indicated that the packing was face-centered cubic. The films produced from ethanol (without ammonia) and heptane systems appeared to have a uniform, random close-packing of particles (this is evident in Fig. 4). The SEMs also show that the thickness variation across films 3 μ m thick was less than 0.5 μ m and that the films did not contain any pinholes.

The SEMs also indicate that the photoresist formed a continuous layer less than 0.1 μ m thick on the surface of the particle film (as shown in Fig. 5), but did not penetrate the particle film. Figures 4 and 6 show the result of the photolithographic patterning process on a layer of silica particles. As these figures show, using this technique, it was possible to produce $5-\mu m$ features in a film 3 μ m thick. Optimization of the photolithographic process and decreasing the particle size should lead to even smaller feature sizes. The figures also show that the variation in line width is on the order of the particle size. This occurs because apparently the photoresist protects the particle film from disruption during sonication by physically separating it from the medium.

Best results were achieved for films deposited from the ethanol and heptane suspension systems. The green strengths of the films produced from the water system were too great to permit easy removal

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Fig. 5. SEM of a patterned silica film covered by a thin layer of photoresist (bar=5 μ m).



SEM of the top surface of a patterned film at low magnification. Fig. 6. The light areas are particle film; the dark areas are substrate $(bar = 1000 \ \mu m).$



Fig. 7. SEM of a patterned film in which the missing regions in the first layer (the thinner lines in the photo) were filled using the technique de-scribed in the text and diagramed in Fig. 2 for the positive-image mask $(bar = 50 \ \mu m).$

during sonication of the silica not covered by photoresist.

Figure 7 shows the result of the technique used to fill in the vacant regions created in the first layer. This sample was made by the more complicated of the two methods described earlier (i.e., using the same type of photoresist and the same mask used to pattern the first layer). The figure shows that lines 20 μ m wide with 30- μ m spacings could be filled quite well. The filling of finer lines, however, was difficult for several reasons. Alignment of the mask over the pattern of the first layer was difficult because this pattern was covered by the second particle layer and the photoresist. Also, even when aligned fairly well there was a tendency for the finer lines to be totally removed during sonication, possibly because when the second film was cast over the first, it bridged over the finer holes in the first without penetrating them and bonding to the surface. This limitation may become more severe as the film thickness increases.

CONCLUSION

A process incorporating photo-

lithographic techniques has been developed to produce patterns in films of ceramic particles. Features with dimensions of only 5 μ m, 10 times the particle diameter, have been produced. This is about 20 times smaller than the minimum feature size which can be produced by either screen printing or mechanical punching. Also, it has been demonstrated that lines 20 μ m wide in the first particle layer can be filled in by modifying the original process. Work is presently under way on modifying this process for use with thicker films and films of nonmonosize particles.

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