Fabrication of Monolithic Sapphire Membranes for High T_c Bolometer Array Development

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ABSTRACT

This paper examines the effectiveness of Pt/Cr thin film masks for the architecture of monolithic membrane structures in *r*-plane single crystal sapphire. The development of a pinhole-free Pt/Cr composite mask that is resistant to boiling H_2SO_4:H_3PO_4 etchant will lead to the fabrication of smooth sapphire membranes whose surfaces are well-suited for the growth of low-noise high T_c films. In particular, the relationship of thermal annealing conditions on the Pt/Cr composite mask system to (i) changes in the surface morphology (ii) elemental concentration of the Pt/Cr thin film layers and (iii) etch pit formation on the sapphire surface will be presented.

INTRODUCTION

The primary motivation for this work is to develop a highly sensitive micro-machined transition-edge bolometer array on sapphire membranes for thermal imaging applications in the spectral wavelength range 20-100µm. Sapphire has several advantages over silicon as a substrate material for the development of high T_c bolometers, in particular, better high T_c film epitaxy resulting in sharper transitions, lower specific heat capacity and higher thermal conductivity at the temperature of operation. However, unlike silicon, sapphire is extremely hard to thin because of its chemical inertness. It would be extremely useful to develop a technique for micromachining sapphire that can be used in conjunction with existing standard photolithographic techniques, for architecturing small area bolometer arrays where each bolometer has an optimized thermal time constant, $\tau = C/G$ where C is the total heat capacity and G is the thermal conductance to a heat sink at temperature T_s. Smaller bolometer areas will result in smaller thermal time constants giving rise to higher temperature excursions in the bolometer film.

Recently, Lakew *et al.* [1] reported on a composite $1 mm^2$ single pixel YBCO bolometer fabricated by thinning a sapphire substrate from 25µm to 7µm in thickness suspended with Kevlar fibers for thermal isolation. This device gave a thermal time constant of 100 ms and a detectivity of 1.2×10^{-10} cm $Hz^{1/2}$/W at 4 Hz. In order to alleviate the need for epoxied Kevlar fibers and eliminate unknowns in contributions to the total heat capacity, it would be advantageous to fabricate monolithic thin membrane structures in thick sapphire frames. This approach will not only result in further bolometer performance improvements (higher sensitivity and faster response time) but will also lead to the long term goal of producing linear arrays while maintaining ease of handling, hybridization and packaging. A notable challenge in the production of bolometers with such an architecture is the design and construction of a pinhole-free mask capable of withstanding boiling H_2SO_4:H_3PO_4 used for bulk sapphire etching[2,3]. Such harsh etch conditions place strict requirements on the materials and methods utilized in the fabrication of an etch mask. An attractive strategy is to use a corrosion-resistant metal such as Pt with a thin, underlying adhesion-promoting layer such as Cr. Subsequent annealing of the Pt/Cr layers should further promote the adhesive

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integrity of the Pt/Cr thin film mask through the formation of a Pt-Cr solid solution[4,5]. This work investigates the effects of thermal annealing on the morphology and structural integrity of Pt/Cr thin film masks. Scanning electron microscopy (SEM), electron dispersive x-ray spectroscopy (EDS) and optical microscopy were used to probe for changes in surface morphology and elemental concentration under different annealing conditions. Implications of the effectiveness of such masks for use in bulk sapphire etching are discussed.

EXPERIMENTAL PROCEDURE

Substrates used in this study were 2" (1-102) sapphire wafers obtained from Kyocera Corporation. Prior to metal film deposition, samples were cleaned and degreased in successive ultrasonic baths of semiconductor grade acetone, methanol and deionized water. Substrates were blown dry with N_2 gas and baked at 120^{o}C for approximately 2 hours.

Pt/Cr layers were deposited using on-axis dc magnetron sputtering from 2" high-purity metal targets mounted in a high-vacuum system. The deposition system was initially evacuated to a base pressure of ~<2E-6 Torr. Deposition occurred near room temperature in an Ar atmosphere. 50 nm of dc magnetron-sputtered Cr was deposited, followed by a cooling period and subsequent deposition of 250 nm of Pt. Thicknesses were measured using a standard Dektak profilometer.

Prior to annealing, samples were examined using optical microscopy, SEM, EDS and atomic force microscopy (AFM). Film surfaces had mirror finishes and were featureless. No defects were found on the surface. The films were shown to be elementally pure and the thicknesses agreed with profilometry results. AFM measurements of the rms roughness of the unannealed Pt/Cr layer = 2.52 nm. The blank substrate had an rms roughness = 0.42 nm.

Samples were annealed *ex situ* in an oxygen atmosphere (flow rate = 10 sccm, scaled to N_2) at atmospheric pressure. Annealing temperatures were selected between 500 - 1000^{o}C. Annealing times were 5, 30 or 60 minutes. Test samples were inserted into an annealing oven pre-heated to 500^{o}C. The furnace temperature setting was increased and the samples were advanced on a quartz sled at until the center was reached. The insertion occurred as the temperature of the furnace was increasing towards the desired setting. Once the sample reached the oven center and the furnace setting stabilized, timing began. The samples cooled to room temperature in an oxygen atmosphere.

RESULTS

Two main types of surface structures were found: blisters and holes *(Figure 1)*. SEM and optical microscopy showed that the density and continuity of these structures is dependent upon annealing conditions. Most specifically, the duration of annealing influenced the density of the surface structures, particularly the number of holes. There was no apparent influence of the annealing conditions on the size of either the blisters or holes that were found on the annealed surfaces.

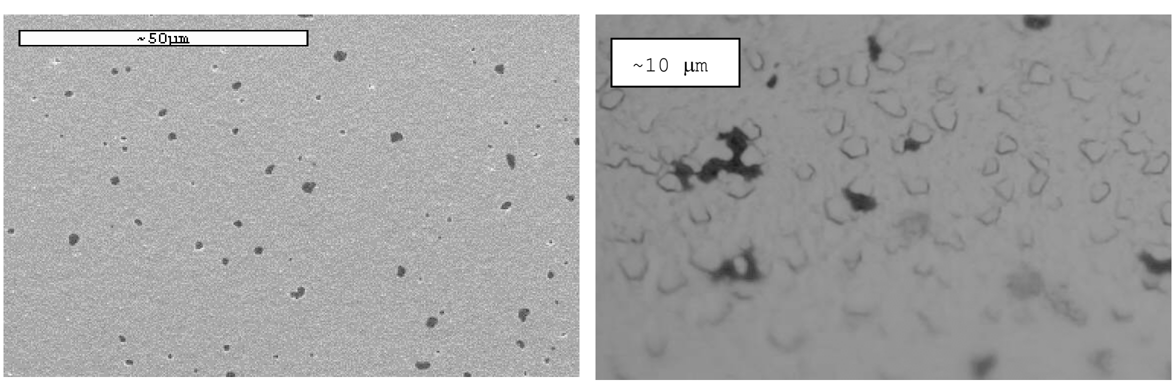

Figure 1: *Scanning electron micrographs of Pt/Cr surface after annealing at 1000^{o}C, 60 minutes for (a) 100 x 100* μm² *square region & (b) 50 x 50* μm² *region. Note the blisters (outlined regions) and holes (solid regions).*

Samples annealed at 1000 ^{o}C exhibited an extensive amount of blistering and holes *(Figure 1)*. The holes found on these samples were likely created by some of the blisters being popped open and exposing the underlying substrate. The holes that appeared on the sample surface had no apparent size limit and a broad range of diameters, indicating that there was no exact critical radius for the blisters to burst open. EDS examination of the regions on the sapphire substrate, beneath the burst blisters showed an insignificant concentration of Cr.

Samples annealed at lower temperatures and/or shorter time (for example, 500 ^{o}C for 30 minutes) exhibited a very limited amount of blistering *(Figure 2)*. EDS detected a small amount of Cr beneath burst blisters found on these samples.

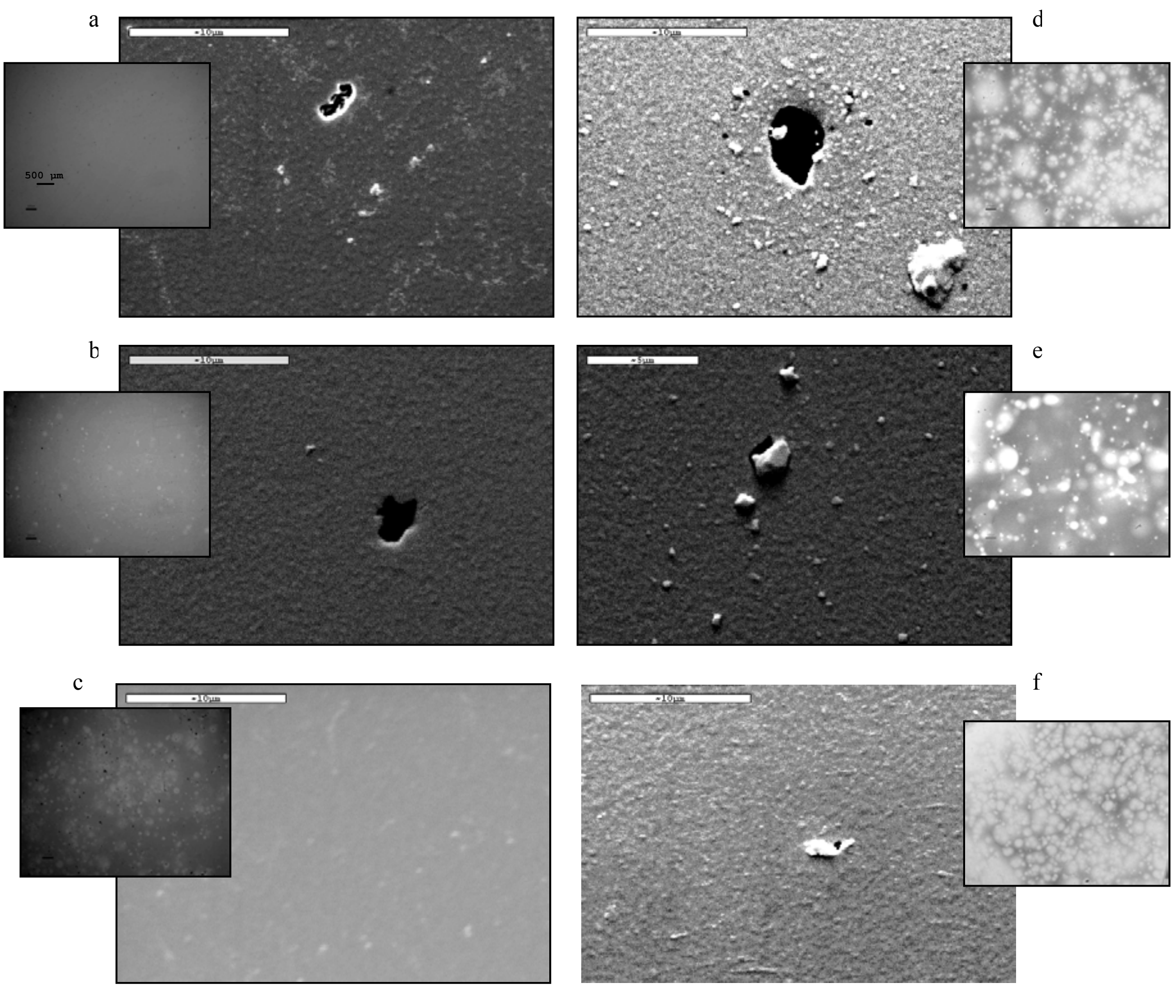

Figure 2 *Scanning electron micrographs of Pt/Cr surfaces, illustrating the temperature and time dependence matrix utilized in this study. Each small inset is an optical micrograph taken for the same annealing condition (scale bar= 400* μm*). Left-side column: samples annealed at 500^{o}C for (a) 5 min, (b) 30 min, (c) 60 min. Right-side column: (d) & (e) samples annealed at 1000^{o}C for 5 min and 30 min, respectively; (f) Unannealed sample. Compare with 1000^{o}C, 60 min micrograph shown in Figure 1(a).*

Away from the blistered regions, EDS showed an increase in surface concentration of Cr with increasing annealing temperature (*Figure 3)*. Some of the chromium (Cr) appeared to have diffused into the platinum (Pt) layer during the annealing and accumulated on the sample surface.

Optical microscope inspection showed increased surface discoloration of the samples with increasing annealing temperature or time *(Figure 2, insets)*. This is likely due to oxidation of the Cr that has diffused onto the surface, as supported by EDS surface data *(Figure 3)*.

DISCUSSION

All samples annealed at 1000°C for 5, 30 and 60 minutes and annealed at 500°C for 60 minutes were blistered. Burst or intact, such features produce a mask which directly permits the entry of corrosives. An intact blister strains the overlying film and may possess fractures at the blister's base. Such fractures may permit corrosive entry. Burst blisters and holes produced by other means provide a direct path of entry for corrosives. Thus, a blistered mask is ineffective for the production of a pit-free sapphire surface.

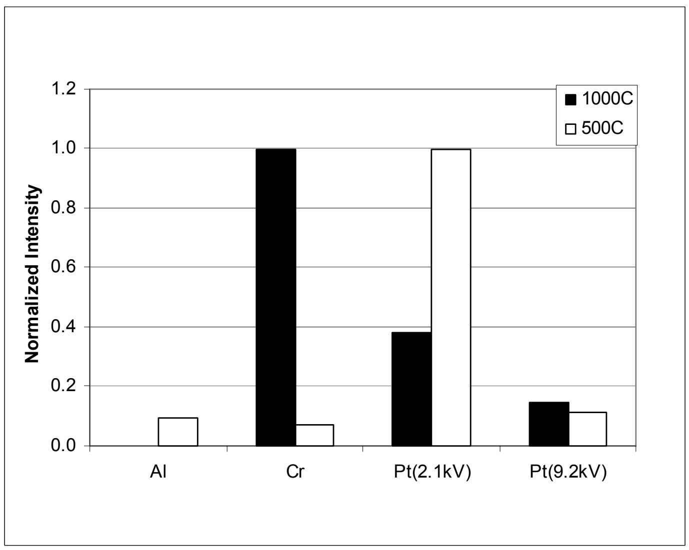

Figure 3: *Comparison of elemental EDS lines for 1000°C and 500°C anneals. Duration of anneal = 60 min. The beam was directed away from blistered regions and holes Data has been normalized with respect to the full scale counts per second setting for a given measurement.*

Annealing as-deposited films composed of a Pt-Cr solid solution results in preferential Cr segregation and oxidation at the films surface. Since Cr is readily attacked by corrosives commonly used in the sapphire etch process, a mask with excessive Cr surface concentration may lose its continuity under standard sapphire etch conditions.

We have determined that surface morphology and composition of the Pt/Cr etch mask significantly influence a mask's effectiveness in sapphire wet etch process. Controlling processing conditions of this etch mask controls the degree to which a mask may be vulnerable or even have its integrity compromised during the etch process. High temperature anneals or anneals above 500°C for times greater than 30 minutes produce a mask that is not pinhole-free, leaving the underlying sapphire vulnerable to pitting by the etchant.

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