Solid-State Bonding Technique for Template-Stripped Ultraflat Gold Substrates

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A simple procedure using gold diffusion bonding for the preparation of template-stripped gold (TSG) surfaces is described. TSG surfaces are useful for surface studies because a very consistent flat gold surface with few defects can be easily prepared. We have developed a method of producing TSG surfaces that relies only on gold diffusion bonding rather than epoxies. The resulting substrates are free from concerns of solvent compatibility, heat stability, and impurities. Bonding of centimeter-sized substrates is performed at 300 °C for 2 h using a vise and aluminum foil.

Introduction

The preparation of flat gold substrates has become important for scanning probe microscopies and in nanotechnology areas such as self-assembled monolayers (SAMs) and SAM-based fabrication. Extremely flat substrates such as mica, polished silicon, and highly oriented pyrolytic graphite are quite useful for scanning probe microscopy studies, but the versatility of SAM chemistry on gold means that flat gold surfaces are in demand for both imaging and fabrication purposes. There have been many reports of methods for producing flat gold surfaces, including direct evaporation of gold onto surfaces,[1−4] template stripping techniques,[5−12] and flame annealing.[13] The template stripping techniques are desirable because they allow for the rapid exposure of a large area of "fresh" gold surface on demand instead of requiring a lengthy evaporation run for each new "fresh" gold surface that is required. However, an easy and reliable method for producing template-stripped gold (TSG) substrates that can stand up to strong organic solvents such as dipolar aprotics has not been reported. In the course of work to produce templated 2D polymers, we required such substrates,[14] and we have found that diffusion bonding using gold can be used for the production of ultraflat TSG substrates. These substrates have solvent and thermal compatibilities similar to those of a typical gold-on-glass substrate.

In the general approach to TSG surfaces, a bonding agent is used to fasten a gold-on-mica substrate to another surface. The mica is then delaminated by solvent or physical stripping, leaving behind the gold surface that was grown on the mica. Because the mica surface is atomically flat over many micrometers, the exposed gold surface is also atomically flat if appropriate gold evaporation conditions are used. Most preparations use an organic epoxy to act as the bonding agent, but the resulting substrates are damaged by some organic solvents, especially with heating.[15] To eliminate organics from the template-stripped substrates, we envisioned the use of a solid-state welding process to make a metal−metal bond. Solid-state welding is a well-studied process that encompasses several different types of joining, including diffusion bonding (thermocompression bonding) and cold welding.[16] Gold-on-gold welding is potentially the most desirable technique for making template-stripped gold films because mixed alloys are not possible.

Recently, Blackstock and co-workers have reported a method for cold welding large-area gold surfaces using silicon wafers to produce template-stripped platinum. Unfortunately, it requires gold surfaces fresh from the evaporator, handled in a clean-room environment and placed in a hydrostatic press within minutes of exposure to air.[17] This method is impractical for the production of multiple substrates on a laboratory scale because of the requirement of "fresh" gold surfaces, and it does not use mica, which is known to give the best gold surface orientation and terracing.[18,19] In contrast, gold diffusion bonding on float glass surfaces across centimeters is readily achieved on aged gold samples,[20] and gold thermocompression bonding is frequently used in the semiconductor industry.[21,22] We were interested in adapting these elevated temperature methods to gold-on-mica surfaces in a manner that could be easily performed in a typical laboratory setting. The difficulty in extending gold diffusion bonding to mica substrates lies in the problem of delivering even pressure to uneven mica substrates over centimeter-sized areas at elevated temperatures. This is a problem for many types of

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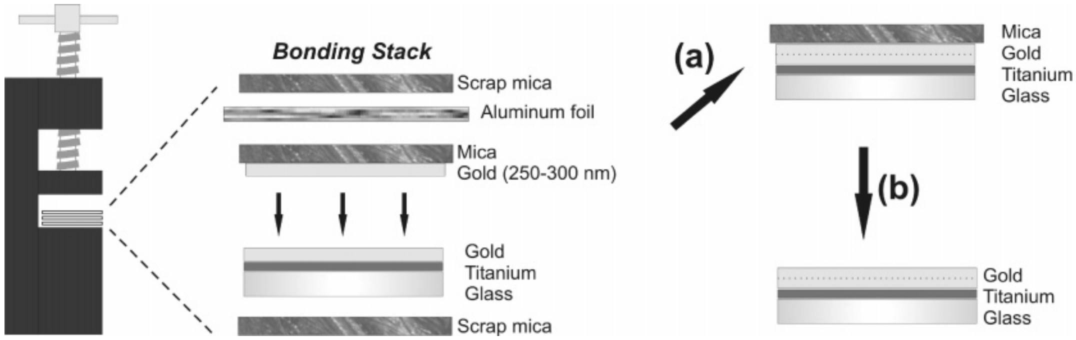

Figure 1. Scheme for template-stripped ultraflat gold substrates made by diffusion bonding. The bonding stack is assembled from a gold-on-mica film, a commercially available gold-on-glass film with a titanium adhesion layer, aluminum foil, and two pieces of "scrap" mica whose purpose is to prevent the stainless steel vise surface from interacting with the glass slide (cracking it) or the aluminum foil (bonding to it). (a) The vise assembly is held at 300 °C for 2 h, and then the bonded mica−gold−titanium−glass substrate is removed. (b) The mica is stripped by soaking in water or prying off with tweezers.

applications requiring even pressure over large areas, such as the case of imprint lithography.[23] We report that simple food-grade aluminum foil can be used for creating even pressure distributions and good bonding across centimeter-sized mica substrates when bonding to gold-on-glass slides. The method requires no hydraulic or hydrostatic presses to achieve the pressures and temperatures required, only a furnace and commercially available machine shop vises. The gold surfaces to be bonded can be prepared by simple solvent washing.

Results and Discussion

Initial efforts to use aged gold surfaces to bond gold-on-mica to commercial gold-on-glass substrates met with limited success. Although the general parameters of pressure and temperature needed are known,[20] we were unable to achieve even gold film transfer across centimeter-sized substrates. Bonding using a vise at 300−450 °C always resulted in only partial gold film transfer onto scattered areas of the gold−titanium−glass substrates. Surface cleanliness, which is crucial in solid-state bonding,[21] was first investigated. Different cleaning approaches, such as plasma or piranha cleaning or using freshly evaporated gold surfaces, did not improve the bonding. Thus, uneven pressure across the mica surface probably limits the intimate contact area between the two gold films. This is due to the uneven thickness of mica substrates, which can be exacerbated by tape stripping or using a razor blade to cleave the mica. Eventually, we found that aluminum foil serves to distribute pressures of 3500−5000 psi across uneven surfaces quite easily. Even mica, which had obvious unevenness, having several different layers onto which gold had been evaporated, bonded quite well.

The recommended bonding configuration is shown in Figure 1. A stack of the two substrates to be bound, the aluminum foil, and additional mica are formed in a small vise. The two extra mica pieces perform the following functions: the lowest mica piece prevents cracking of the glass slide due to thermal mismatch with the stainless steel vise, whereas the uppermost mica piece prevents the aluminum foil from binding to the vise surface. We use a torque wrench to obtain consistent pressures from film to film and calibrate with pressure-sensitive paper.

The malleability of the aluminum foil allows the creation of high pressure across the uneven bonding stack during compression of the vise. After use, the aluminum foil surface becomes shiny and mirrorlike in the areas of maximum pressure, indicating that the foil is compacted by the bonding step. Using the same aluminum foil layers a second time does not result in even gold bonding, and using too few layers of aluminum foil results in poor bonding (Supporting Information). The thermal expansion coefficient of aluminum is higher than that of any other component in the vise−gold substrate system, which might explain the improved bonding. However, aluminum sheets ($^{1}/_{16}$ in. thick) do not equalize pressure adequately in this system and lead to poor bonding across a 1.5 cm^2 substrate. This implies that a high thermal expansion coefficient alone is not adequate for the desired effect. In addition, foils with thermal expansion coefficients similar to or slightly lower than those of the cast steel vise—nickel, tin, and copper—also create even bonding at elevated temperatures. These results indicate that compaction, which is densification of the metal foil layers by removal of the voids and ridges found on the foil surfaces, may be the primary process that leads to even pressure distribution on the mica substrates.

Using pressures of 3500−4000 psi, we find that excellent transfer of films occurs over a wide range of temperatures, although more time is required for lower temperatures. Bonding occurs at 400 °C (1 h), 300 °C (2 h), and 200 °C (4−6 h). Less reliable bonding occurs at shorter times at these temperatures. Bonding at 100 °C gives only partial transfer after 18 h. The pressures employed in this study for gold bonding are around 10 times the pressures reported for gold thermocompression bonding on silicon, and the time scales are also longer.[22] Longer bonding times are needed with this technique because we are using aged gold surfaces in a laboratory setting.

Removal of the mica to expose the atomically flat gold surface of these TSG substrates is accomplished by solvent or manual stripping. It should be noted that in some cases partial delamination of mica from the gold surface occurs upon removal from the vise. This is due to the high interfacial stress between the gold layer and the mica layer. In these cases, the mica is then fully removed by prying off with tweezers. If the mica is not manually stripped from the gold surface, then water or ethanol can be used. Water loosens the mica surface so that it may be gently pulled off, and often the mica spontaneously separates from the TSG surface. The separation of the mica/gold interface is driven by thermally induced stress at the interface, as in the liquid-nitrogen release technique of Mazurkiewicz and co-workers.[7]

As shown in Figure 2, the defects of the mica surface are transferred to the TSG substrate, showing up as visible ridges of gold surrounded by smooth surfaces. Ridges are from multiple mica layers being exposed on the mica surface during the evaporation of gold onto the mica. By carefully cleaving and selecting mica before evaporation, these types of defects can be prevented if desired. Some point defects are usually present on substrates as well, evident in Figure 2, which are likely due to

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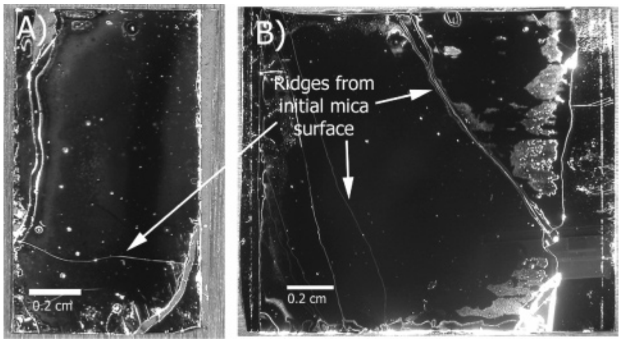

Figure 2. Optical images (dark field illumination, 0.2 cm scale bar) of TSG substrates made by gold diffusion bonding after mica lift-off are shown. The TSG substrates show ridge defects from the mica layers on the initial Au/mica substrate, as marked. On each substrate, defects from dust particles are also evident as white circular point defects. The large defects at the edges of both substrates are typical and are due to uneven pressure at the edges in the vise stack. Substrate A was bonded at 300 °C for 2 h, and substrate B was bonded at 200 °C for 6 h.

dust particles in the bonding step. In the case of the largest substrates we have used, 1.5 cm × 1.5 cm, sometimes there is a slight white haze visible to the eye on the exposed TSG surface. This haze is due to large pits in the TSG surface caused by excessive stress at the gold/mica interface. The haze can be eliminated in larger substrates by bonding for 6 h at 200 °C rather than for 2 h at 300 °C.

Figure 3 shows tapping-mode atomic force microscopy (AFM) images of a gold-bonded TSG surface. Triangular and aligned steps on the gold surface are common on these substrates. The presence of terraces formed from 60 and 120° angles indicates the relief of strain through slip along a (100) glide plane.[4] The steps caused by the (100) glide planes are often several gold atoms high (atomic diameter 0.288 nm), measuring from 0.5 to 1.1 nm in height. The presence of triangular terraces is good verification that the surfaces are (111). As shown in Figure 3C, the triangular steps from release of strain are superimposed on the wavy gold steps which are expected due to an epitaxial mismatch between the gold and mica surfaces. The root-mean-square (RMS) roughness of these surfaces is typically 0.5−0.6 nm over 5 micron areas, and ranges from 0.2 to 0.5 nm RMS roughness over 1 micron areas, which is in line with other literature reports. Submicron sized holes are often seen in TSG surfaces created by high-temperature evaporation,[5−7,10] and our surfaces show holes with depths ranging from 2 to 20 nm.

The production of optimal TSG surfaces from solid-state welding requires the integration of the correct annealing times and evaporation conditions for the gold-on-mica substrate. Although the use of pressure during bonding has no discernible impact on TSG morphology versus epoxy techniques, the thermal history of the sample is important because the gold atoms can rearrange at elevated temperatures, altering the resulting TSG surface. The gold on mica substrates should be prepared by thermal evaporation at substrate temperatures of 300 °C and at an initial gold evaporation rate of 0.5−1 nm/s.[24] An extensive mica prebake step before evaporation is not required as long as the substrates are at the appropriate temperature at the beginning of the evaporation. The *initial rate* of evaporation must be in the range of 0.5−1 nm/s. If the mica substrate is exposed to gold evaporation at lower rates initially, then the gold forms islands on the mica surface, resulting in a high number of defects on the TSG surface. Likewise, initial rates that are too high, >2 nm/s, lead to significant roughening of the TSG surface. Finally, the gold-on-mica substrates should not be annealed at temperatures above 250−300 °C for longer than 4−6 h after evaporation, or large defects on the TSG surface result. This time includes the gold bonding step also, which is performed for 2 h at 300 °C.

We have not done significant bond strength testing but find that these substrates survive the "tape test." Regions that are poorly bonded because of poorly cleaved or very uneven mica do delaminate with tape. X-ray photoelectron spectroscopy of TSG substrates has shown no evidence of residual mica or of titanium diffusion from the adhesion layer of the glass slides to the template-stripped surface (Supporting Information). We have used these TSG substrates for SAM formation and soft lithography patterning with no issues.

Conclusions

An easy and reproducible method of preparing TSG surfaces from gold-on-mica has been developed. Because no epoxies are involved, the resulting TSG substrates are quite useful for studies involving organic solvents, and the user is assured of no organic contamination due to the TSG technique. This preparation allows the production of TSG surfaces with minimal extra effort because the surfaces need only a solvent wash and a compression step with a wrench. Diffusion-bonded TSG surfaces are the most robust ultraflat gold surface developed to date.

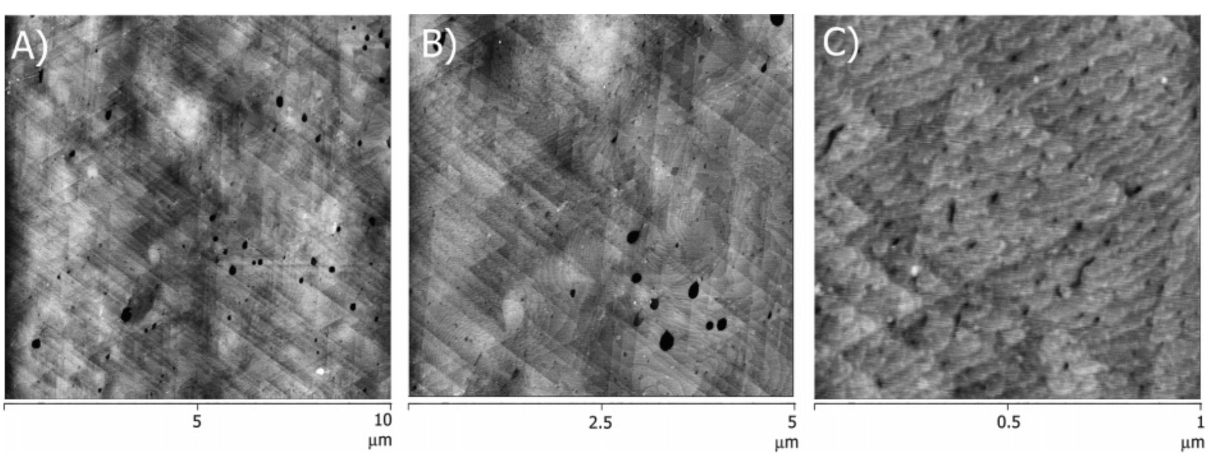

Figure 3. Tapping-mode AFM images of a TSG substrate made by gold diffusion bonding at 300 °C for 2 h. The *z*-height scale for A and B is 5 nm, and that for C is 3 nm. Scans A and B show that large areas of the gold surface consist of aligned step edges on the gold surface, some of which intersect to form triangular features. The step-edge features, which are from 1 to 3 atoms high, are due to glide along the (100) planes in the Au lattice. Scan C shows that these aligned step edges are superimposed on the wavy atomic steps, caused by a small epitaxial mismatch between gold and mica, which are expected at the gold−mica interface.

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(24) It is important to use gold on mica films that have been evaporated at a substrate temperature of 300 °C. Substrates that have been deposited at room temperature undergo a massive reorganization due to annealing during the 300 °C bonding step.

Supporting Information Available: Photographs of the vise apparatus and bonding results, experimental details, an additional AFM, and an XPS spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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