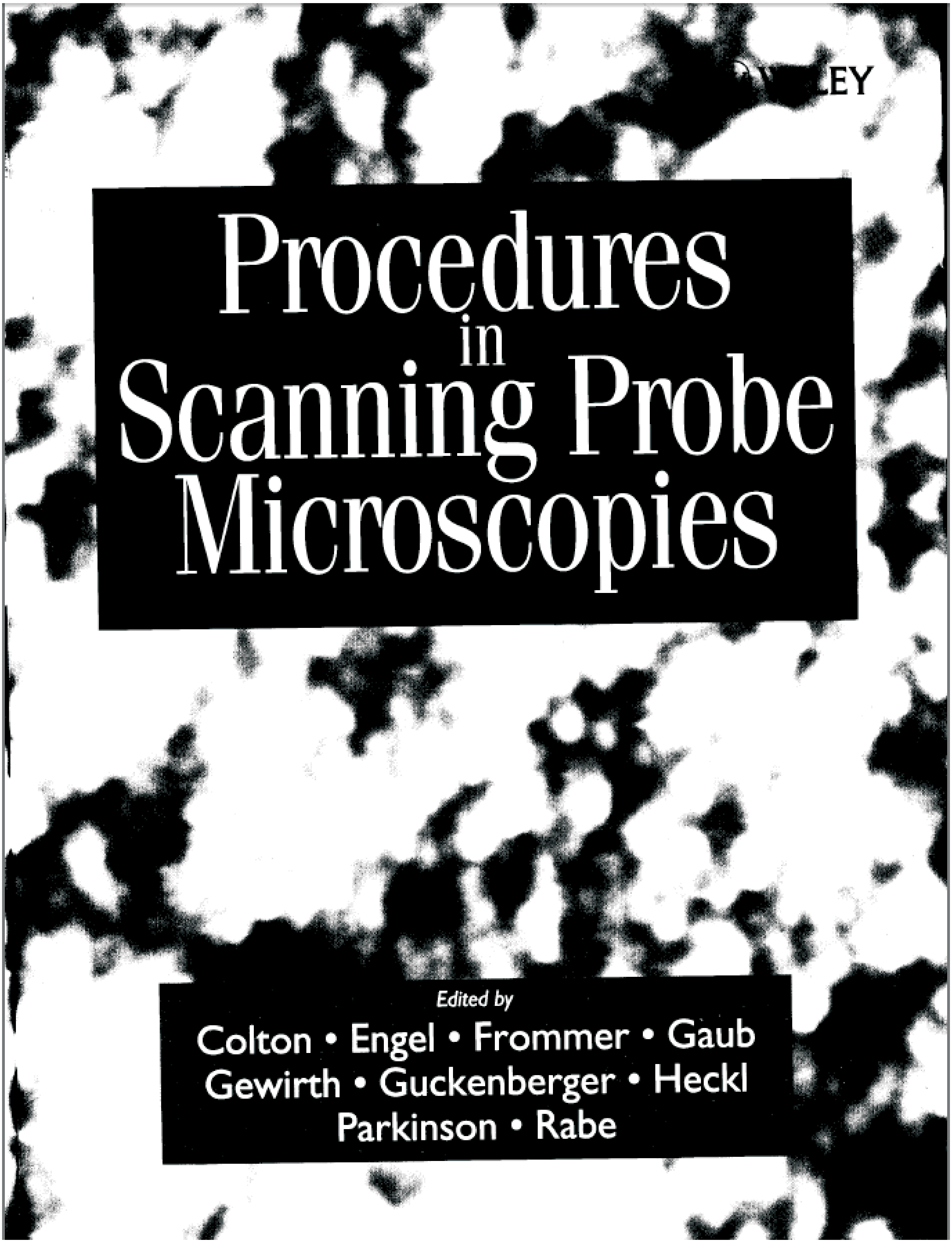

Procedures in Scanning Probe Microscopies

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Module 2:2:4 Ultraflat Au surfaces

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In this module, a simple method to produce a well-characterized, ‘atomically’ flat substrate is presented. Chemical and physical properties of the substrate are of primary importance. In addition to being chemically inert against O_2 (but endowed with specific chemical reactivity) the substrate must be atomically flat over large areas; otherwise objects having unfavourable length:width ratios will "sink" into an irregular topography. This is especially true for fibrillary structures of µm length, *e.g.*, nucleic acids or organic polymers with diameters smaller than 3 nm, but also for individual globular proteins. These macromolecules require substrates with a mean roughness as small as a few Å on areas of at least 5 μm^2. Finally, the ideal substrates should also be reasonably priced and easy to prepare, to store, and to chemically modify.

Gold is a popular substrate. It is stable against O_2, can be easily prepared by vapor-deposition, and can bind with high affinity organic thiols or bifunctional disulfides such as gold(I)alkanethiolates ($RS^-Au(I)$) (see module 5.3.1 and module 7.12.2) also capable of forming self-assembled monolayers. The epitaxial growth of f.c.c. metals on mica as a substrate is well known, and polycrystalline gold films which form with (111) orientation on the (001) cleavage planes of mica have been extensively studied [3-5]

Au surfaces prepared by the above procedures suffer from a number of imperfections (see, *e.g.* [5]). The terraces obtained by depositing Au on mica at optimal temperature, *i.e.*, 300 °C - 500 °C, which is the most widespread technique, have varying sizes and are surrounded by unpredictable and rough topography (see Fig. 3a). Indeed with deposition at constant temperature it is impossible to avoid the formation of deep depressions. Hence these are useful only for macromolecules which are smaller than the terraces themselves. Other Au surfaces (*e.g.*, single crystals, annealed gold balls, *etc*.) suffer likewise from various limitations, such as high cost or lengthy preparation procedures [5]. Finally, all Au surfaces described thus far have to be prepared immediately before use, which is time-consuming for routine use.

We have developed a simple procedure to reproducibly prepare ultraflat template-stripped gold surfaces (*i.e.*TSG)(see Fig. 3b-d). The procedure is described in this module. An additional practical advantage of this technique is that the gold surfaces can be quickly obtained from their immediate precursors, which are stable and can be prepared and stored for months in bulk.

Procedure Preparation of template-stripped gold (TSG)

A method has been devised to produce µm-sized gold films with 'atomically' flat areas for use in scanning probe microscopy [3]. A mean roughness of ~ 2 Å for areas of 2.25 μm^2, and about 3 Å for 25 μm^2, can be easily produced.

The method is based on (see Figure 1):

1. Epitaxial growth of gold on mica. Gold is deposited onto freshly cleaved mica sheets by thermal evaporation.
2. Glueing the gold surface onto a piece of Si wafer or glass coverslips.
3. Chemical stripping of the mica down to the appearing gold surface (TSG).

MATERIALS

- Gold (99,99%) or (99.999 %), *e.g.* from Cendres & Metaux SA (Biel, Switzerland) or Goodfellow Cambridge Limited (Cambridge, UK).
- Muscovite mica: Provac AG (Balzers, Liechtenstein) or Goodfellow Cambridge Limited (Cambridge, UK).
- Small pieces of monocrystalline Si(100) wafers or glass coverslips Suppliers include Wacker-Chemtronic GmbH (Stuttgart, Germany) and Plano, W. Plannet GmbH (Marburg, Germany).
- Low-viscosity epoxy glue epo-tek® 377. Suppliers: Polyscience (Cham, Switzerland) and Epoxy Technology Inc. (Billerica, MA, USA)
- Tetrahydrofuran (THF) commercial grade of highest purity.

EQUIPMENT REQUIREMENTS

High vacuum coating system for thermal evaporation with integrated quartz crystal deposition controller (vacuum during deposition < 2,66 X 10^{-4} Pa). The mica sheet has to be radiatively heated in situ from the rear (temperatures 20 °C to 400 °C).

SAMPLE PREPARATION

Preparation of the gold films:

1. Cleave the muscovite mica sheets (~5 x 7 cm) with a glaucoma knife (without using water) and place them immediately cleaved side down into the sample holder of the vacuum system.

2. Heat the mica sheet *in situ* from the rear through the sample holder, with temperature feedback control through a thermocouple. After twenty hours at 300 °C at a pressure of less than 1.33 x 10^{-4} Pa, equilibrate 30 minutes at the substrate temperature chosen for the gold deposition , *i.e*. 20 - 25 °C or 300 °C.

Note: The temperature finally adopted for our routine work is 300 °C; see [3]. Carry out the evaporation of the gold at a pressure of less than 2.66 x 10^{-4} Pa.

3. The deposition rate should be adjusted to 1 Å/s before opening of the shutter! Evaporation rate should be 1 Å/s and the film thickness ~200 nm to increase the mechanical stability for stripping.

4. Close the shutter and anneal the samples for 2 - 6 hours at 300 °C. Cool slowly down to room temperature (10 °C / min). After removal from the evaporation chamber it is not necessary to store the gold films under special protective conditions.

Note: In our system the resistively heated tungsten boat for thermal metal evaporation is 25 cm directly below the mica substrate.

5. Cut the gold deposited mica sheets into small pieces (~1 cm^2) and glue them face down onto Si(100) wafer pieces or glass coverslips using the epoxy glue epo-tek® 377. Heat the multilayer at 150 °C for 1-2 hour until the glue reaches an adequate hardness. This Si-Au-mica multilayer can be stored as a "stripping precursor" at least up to several months without loss of quality.

Comment: Don’t use other epoxy glues! The glue should be exactly [±10 mg] weight out (w/w (!); 1:1) on a balance and thoroughly mixed. A surplus of epoxy glue should be avoided. For a 1 cm^2 piece use 10 - 15 µl of mixed glue.

Stripping:

We had seen in preliminary experiments that soaking the Si-Au-mica multilayer in various solvents lead to detachment of the complete mica-sheet from gold-Si ("chemically stripped gold surface") without undue effect on the gold surface.

1. Soak the mica-gold-Si "sandwiches" in tetrahydrofuran (THF) at room temperature. Check every two minutes with a vacuum suction (outside of the solvent, *~20-30 mm Hg*) from the top whether the mica sheet separates from the gold surface.

2. Rinse the freshly stripped gold surface with 5-10 ml THF.

3. Check the conductivity with a voltmeter.

Comment: Use fresh glassware for each stripping procedure. The template-stripped gold surfaces should be immediately used for biological experiments or for the modification with a (bioreactive) self-assembled monolayer reagent (see module **7**.12.2). X-ray photoelectron spectroscopy (XPS) analyses showed that only trace amounts of Si and Al from the original mica were left on the Au(111) surface (data not shown). The Si-gold multilayer (prepared with epo-tek® 377) is stable for days in aqueous buffer, alcohols, 1,4-dioxane, and others for hours.

SPM measurements:

The measurements can be performed under ambient conditions on a commercially available scanning tunneling or atomic force microscope.

CONCLUSION:

In summary, the template-stripped gold surfaces prepared by our stripping procedures seem to be superior to other Au(111) surfaces in several respects: (i) they are very large, with very low roughness over extended areas (see Fig. 2); (ii) they are easy to prepare, and (iii) can be made immediately before use from the gold-covered mica specimens; these are stable for months and can thus be prepared and stored in bulk. Images such as that in Figure 3b)-d), which were obtained routinely, make our template-stripped surfaces highly suitable gold substrates for scanning probe microscopy.

Finally, our template-stripped gold surfaces are well-characterized potential alternative substrates for nanolithography by scanning tunneling microscopy

References

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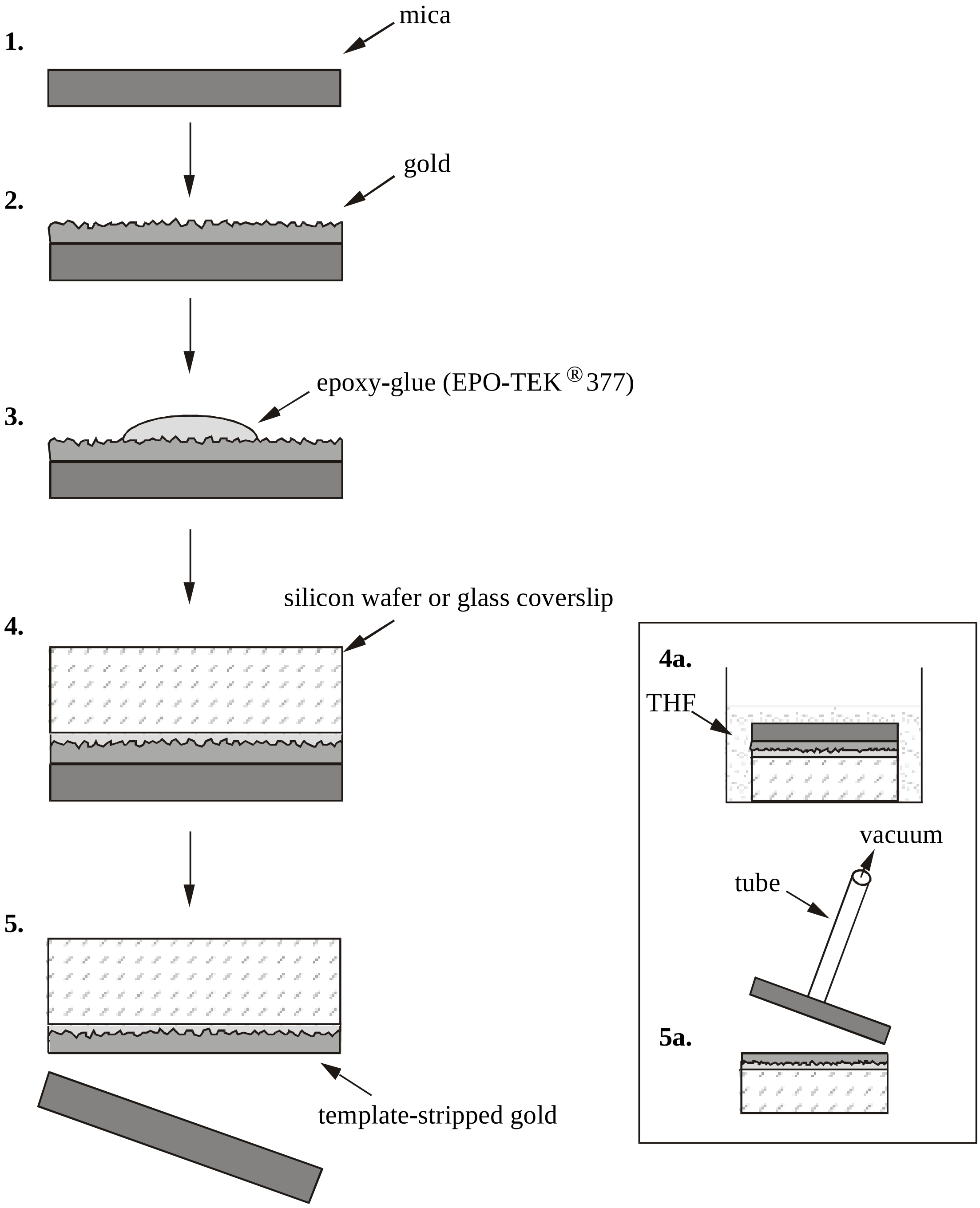

Figure 1 Scheme of the procedure

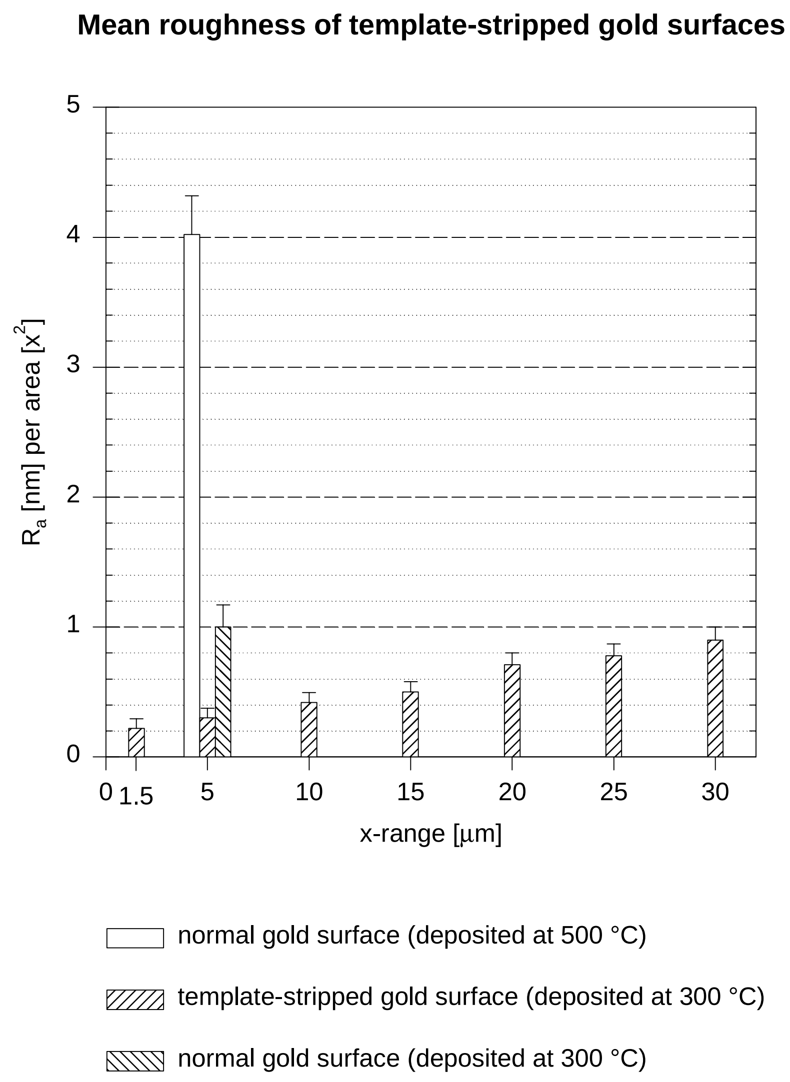

Figure 2 Mean roughness values of the normal and the template-strippedgold surfaces of the same specimens over an area of (x^2 µm^2)

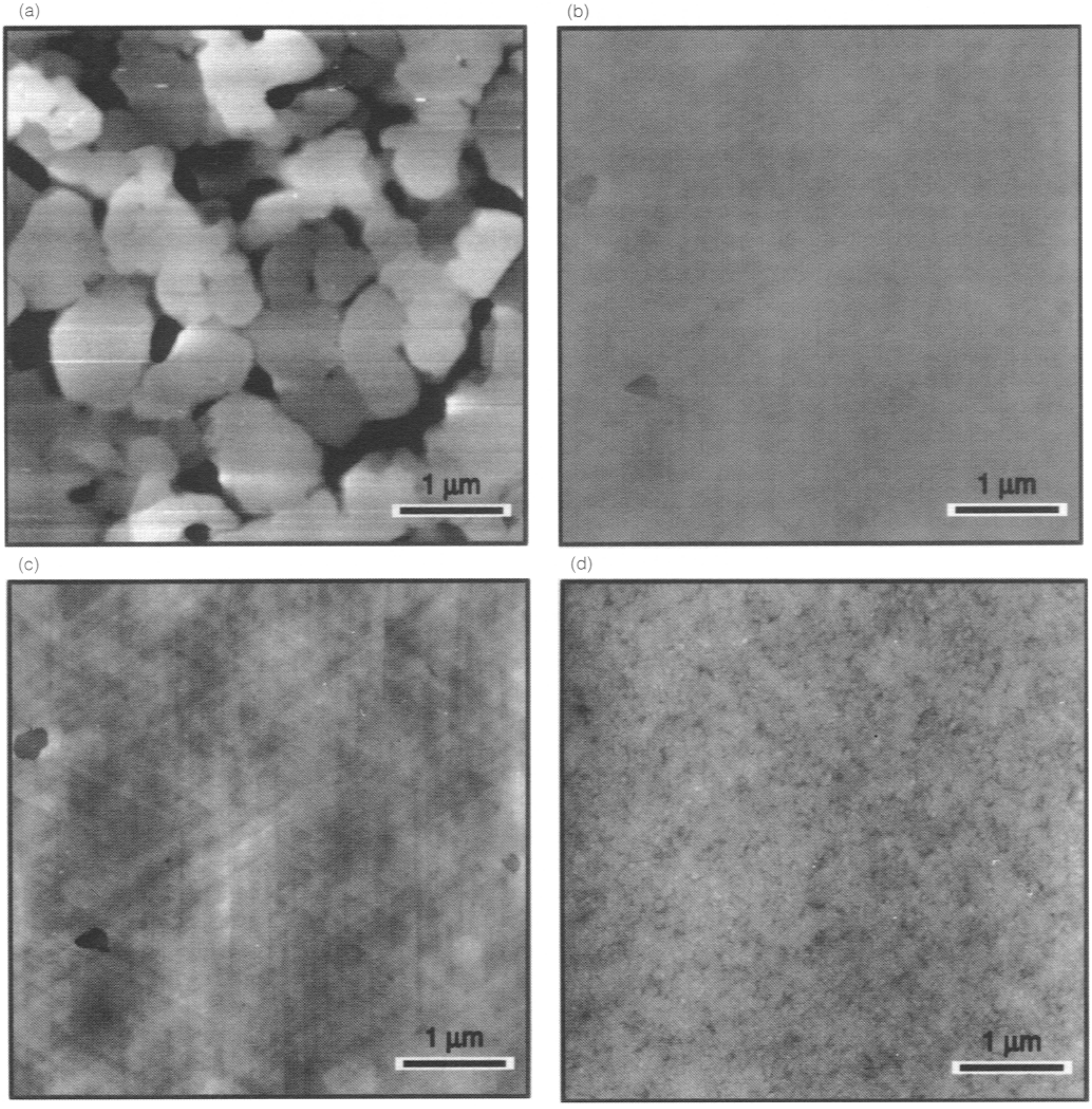

Figure 2.2.4.3. a) STM topview of a 'normal' gold surface deposited at 500 °C. 5 μm × 5 μm, z-range 50 nm; b) STM topview of a template-stripped gold surface deposited at 300 °C. 5 μm × 5 μm, *z*-range 50 nm; c) STM topview of a template-stripped gold surface deposited at 300 °C. 5 μm × 5 μm, *z*-range 4 nm. (to visualize better contrast); d) STM topview of a template-stripped gold surface deposited at 20 °C. 5 μm × 5 μm, *z*-range 4 nm.