

Method for recoating phosphor on commercial low-energy electron diffraction optics

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We describe a method for applying a new coat of phosphor to a commercial low-energy electron diffraction screen. The method is based on sedimentation of a phosphor suspension onto the screen.

Evaporation of thin films within ultrahigh vacuum can lead to degradation of vacuum components. It has been our experience that the most noticeable degradation occurs in the phosphor-coated screen which is usually present in standard, commercial optics for low-energy electron diffraction (LEED), even when the optics are shielded from direct line-of-sight with the evaporation source. This problem (and others, such as cracking, staining, or development of dark spots) can be remedied by coating the screen with a fresh layer of phosphor. Knowledge of how to do this is not common among those who work with such equipment. This note describes a recoating technique based on sedimentation of a phosphor suspension onto the screen. It is a variant of a technique originally developed to coat cathode-ray tubes, television picture tubes, and similar devices.¹⁻³ We have used this procedure successfully several times on commercial Varian screens.

The choice of phosphor deserves special mention. An obvious criterion is the spectral output of the screen, relative to the sensitivity of the detector. Phosphors are classified as P1, P2, etc. based upon the characteristics of their fluorescent and phosphorescent emission.^{1,2} The luminous output of a LEED screen during operation of the electron beam is, by definition, fluorescence.^{2,3} Commercial Perkin-Elmer LEED optics contain a P1 phosphor, with green fluorescence; Varian optics use a P4 phosphor with blue-white fluorescence. The human eye is commonly used as a detector; its sensitivity peaks at 5600 Å, in the green-yellow region of the spectrum.³ If a video or photographic camera is used as detector then its spectral sensitivity should also be considered in choosing the phosphor. For instance, silicon-intensified-target (SIT) cameras commonly have maximum sensitivity at 4500 Å, in the blue region of the spectrum. Another criterion is the suitability of the phosphor for the sedimentation process. For the sake of obtaining a uniform suspension of phosphor particles, it is desirable to use a material with a narrow particle-size distribution and few agglomerates.

One phosphor we have used is RCA-33-Z-151M, a zinc sulphide base activated with Ag. This material is commonly used for black and white television screens, and has blue emission in LEED. The particles of this phosphor are rounded polyhedra ranging from 1.5 to 6 μ in diameter. There are, however, many clusters which range in size from 15 to 30 μ. The phosphor we prefer is Lumilux[®]

Yellow-Green B20-1B, a P20 phosphor available from Riedel-DeHaën AG, Wunstorfer Str. 40, D-3016 Seelze 1, Hannover, Germany. This exhibits a yellow-green emission to which the human eye is much more sensitive. Because this phosphor contains beryllium, the same precautions should be taken in its handling as those recommended for powdered or dissolved beryllium.⁴ The Lumilux[®] phosphor consists of highly spherical particles with a more uniform size distribution, 2-3 μ. Again, however, clusters of 15-30 μ are present.

The procedure has four basic parts: pretreatment of the LEED screen, solution preparation, sedimentation draining, and drying-inspection. In our laboratory, a typical schedule for the entire procedure is: day no. 1 for screen and solution preparation; night no. 1 for sedimentation; day no. 2 for draining; night no. 2 for room-temperature drying; and the morning of day no. 3 for inspection and screen baking. It is helpful to prepare the screen and the sedimentation beaker before preparing the solutions. Before starting, several items must be available. The first is an ultrasonic bath or ultrasonic disruptor. If the former, it should be large enough to contain a 1 ℓ Erlenmeyer flask. The second is the sedimentation beaker, which has a stopcock joined to the bottom center or bottom side, as shown in Fig. 1. We use a 3 to 5 ℓ beaker. The third is an oven for baking the coated screen at 80 °C.

The quantities and sizes given throughout this article assume a final total volume of 3 ℓ, adequate for a Varian 981-0129 screen. However, the amounts and sizes can be adjusted proportionately to meet different requirements of total volume. All water, including rinse water, should be deionized and distilled; all glassware should be clean and dust-free.

Pretreatment of LEED screen: In commercial, front-view LEED optics the fluorescent screen is made of a phosphor-coated aluminum or stainless steel surface. The Varian 981-0129 model, for instance, is made of stainless steel. An old coating of phosphor can be removed easily by wiping it off with a cloth, then degreasing the metal substrate with methanol or acetone. (However, an old coating may contain Be, and appropriate precautions should be taken.⁴) A pickle is then necessary to obtain good adhesion of a new coating. All pickles described here involve HF, for which special safety precautions should be observed.⁵

One of two pickles may be used for stainless steel: (i) 30

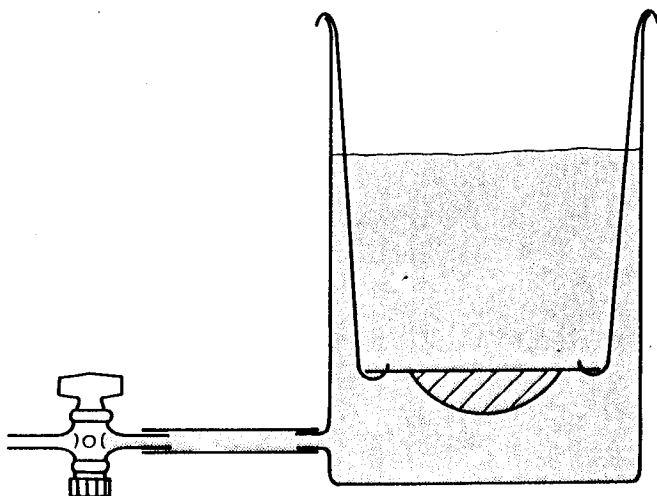


FIG. 1. Schematic drawing of the sedimentation beaker, with the LEED screen suspended. The stopcock can be glassblown in place or coupled to the beaker via flexible tubing, as shown.

(vol) % HNO_3 and 3% HF. Warming this solution will quicken its action; immerse screen for 30–60 s. (ii) 100 ml HNO_3 , 20 ml HF, 20 ml HCl, and 800 ml warm water. Immerse screen for 5 min in an ultrasonic bath.

If the screen is aluminum, dip for 20 s in a 6% HF solution. Rinse with water. Dip for 60 s in 32% HCl. Do not dip for longer times. If the aluminum turns black in the HCl solution, repeat the HF and HCl dips.

Solution preparation: Prepare two solutions as described below. Always cover the solutions to protect them from dust.

Solution 1: 300–500 ml water; 1.8 g $\text{Ba}(\text{NO}_3)_2$ (an electrolyte which effects the gelation of the phosphor particles with the silicate¹).

Solution 2: 150–175 ml water; 0.18 g silica gel⁶ (to act as a binder¹); 3.2 g phosphor.

The object of the following procedure is to get a homogeneous solution of small, fine phosphor particles. A large ultrasonic bath is necessary. A sonic disruptor (also called an ultrasonicator, but not the same as an ultrasonic bath) may be used as well, and is recommended for phosphors which contain many clusters, such as the RCA preparation. Do not let the phosphor solution stand; continue immediately with the next step to prevent settling. Never place a volumetric flask in an ultrasonic bath with the flask sealed by a stopcock, as vibrations may wedge the stopcock so tightly that it becomes impossible to remove.

Solution 1: Add the $\text{Ba}(\text{NO}_3)_2$ to the water in an Erlenmeyer or volumetric flask. Shake vigorously by hand for 2 min. Place in the ultrasonic bath until ready to use, anywhere from 10 min (minimum) to 2 h. Check the bath temperature regularly and replace the bath with cool water as necessary to maintain room temperature. Also, periodically shake the solution vigorously by hand. Shake vigorously before using.

Solution 2: Mix the the silica gel⁶ and phosphor with the water. If using a sonic disruptor, prepare the solution in a

beaker and stir vigorously with a magnetic stirbar while using the disruptor for a total of ~10 min. If using an ultrasonic bath, prepare the solution in a volumetric or Erlenmeyer flask and shake vigorously by hand for ~2 min before placing in the bath. Use the bath for five minutes, stop to cool the bath and/or shake the flask, and return to the bath for 5 min.

Transfer the phosphor solution into a large Erlenmeyer (≥ 1 l) and dilute to 500 ml with water. Use a squirt bottle to completely transfer the solution from the beaker/flask. Add the $\text{Ba}(\text{NO}_3)_2$ solution, using water to rinse and make a final volume of ~1 l. Shake vigorously by hand 1–2 min. Place in the ultrasonic bath for 10 min. Shake vigorously again by hand for 1–2 min. Pour the solution into a 3 or 4 l beaker. Rinse the flask several times with water, adding the wash to the beaker. Fill to 3 l with water. Using a large (~3 in) stirbar, stir rapidly for 5–10 min. When the vortex disappears, let the solution settle (covered) for 10 min. This allows the sedimentation of large particles; if the settling period is longer, fine particles will settle as well, which is undesirable. Decant the solution into another beaker, being careful to leave the bottom of the solution undisturbed, and leaving enough solution behind to avoid pouring out larger particles. Cover the decanted solution and let settle for 7 min. Using a funnel, and directing the solution away from the screen, carefully decant this solution into the sedimentation beaker (in which the LEED screen is already suspended, as described below). Pour evenly and continuously to avoid introducing air into the solution. Trapped air may form bubbles which adhere to the LEED screen.

Sedimentation and draining: The sedimentation beaker is a 3 l beaker with a stopcock joined to the bottom, either glassblown in place or connected via flexible tubing, as shown in Fig. 1. Set the beaker on a ringstand or other appropriate holder, as level and vibration-free as possible. Suspend the LEED screen about 3/4 (or slightly more) of the distance to the bottom of the beaker using three hooks of stainless steel wire. Attach the hooks to the screen through the holes near the perimeter of the screen, and bend them around the sides of the beaker (see Fig. 1). Do not support the screen in any other way. The goal is to allow no disruption in the flow of solution past the screen during draining. The hole in the screen for the electron gun invariably leaves a lingering drop which depletes/disrupts the coating around the hole. A level screen makes this area as small and symmetric as possible. Cover the beaker.

The solution should stand for 5–12 h, until very clear. During sedimentation the beaker should not be accidentally touched, and vibrations should be reduced to the minimum level possible. After this period, carefully adjust the stopcock until the solution just begins to drip out. Do not disturb the solution in any way, as the coating is very fragile at this point. Set the flow rate to drain the entire solution in 6 or more hours.

Drying and inspection: After draining the solution, let the screen stand (covered) several hours. When it appears dry, inspect it for homogeneity. A visible "ring" on the screen indicates a discontinuity in the thickness of the coat-

ing. This probably results when the drip rate changes abruptly during draining, perhaps due to a particle becoming trapped in the stopcock. Other flaws may include particles, dust, bare spots, or thin patches. Depending upon their severity and the type of measurements for which the screen will be used, such flaws may necessitate restarting the procedure. If the screen looks acceptable, remove it from the sedimentation beaker and bake for 30 min at 80 °C. Keep the screen covered at all times. Inspect the screen again.

In our experience, this procedure provides a layer of phosphor-plus-silica $\sim 10 \mu$ thick, which is well-suited for LEED measurements. If a thicker coat is desired, the sedimentation process may be repeated. However, each time the process is repeated there is a risk of "lifting" the previous coating, especially while filling the sedimentation beaker. It may be better to restart the procedure with more solution, or with a more concentrated solution. A coating which is too thick may result in charging effects, particularly problematic if the screen is to be used as a retarding field analyzer in Auger. We also find that outgassing from the recoated screen in ultrahigh vacuum is not problematic; good base pressures ($\leq 2 \times 10^{-10}$ Torr) are typically achieved after a normal, mild bakeout ($T < 150$ °C for 24 h) in a standard stainless-steel, ion- and turbo-pumped system. Furthermore, mass spectrometry indicates that the distribution of background gases does not change significantly as a result of recoating the screen.

In summary, we have found this to be a useful procedure for recoating commercial LEED optics.

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¹F. Rosebury, *Handbook of Electron Tube and Vacuum Techniques* (Addison–Wesley, Reading, MA 1965), pp. 251–254.

²J. Millman, *Vacuum-Tube and Semiconductor Electronics* (McGraw–Hill, New York, 1958), p. 41.

³K. R. Spangenberg, *Vacuum Tubes* (McGraw–Hill, New York, 1948), pp. 429–432 and 821.

⁴Data Sheet 562-Revision A, "Beryllium," National Safety Council, 444 North Michigan Avenue, Chicago, IL 60611, 1972.

⁵Data Sheet I-459-Revision 86, "Hydrofluoric Acid (Aqueous)," National Safety Council, 444 North Michigan Avenue, Chicago, IL 60611, 1986.

⁶A silica gel we have used is Davisil 62 from Davison Chemical (a division of Grace Chemical), Baltimore, MD 21203. This consists of porous, somewhat spherical particles in the size range 75–250 μ . The surface is hydroxylated; the total surface area is $\sim 300 \text{ m}^2/\text{g}$; and the pH is 7. The chemical composition is 99.8% SiO₂. In general, silica gels have smaller particle sizes than silica powders.