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JET THINNING OF GERMANIUM FOR TEM USING AUTOMATIC TERMINATION OF POLISHING*

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JET THINNING OF GERMANIUM FOR TEM USING AUTOMATIC TERMINATION OF POLISHING*

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Abstract

This report describes an automated jet electropolishing technique, using modified commercial equipment, for the production of germanium TEM specimens. This technique allows rapid and reliable thinning of large areas and results in clean surfaces.

1. Introduction

Semiconductor materials such as polycrystalline germanium have been tedious and expensive to thin for transmission electron microscopy (TEM) work, especially when large quantities are needed. This is due to the labor required to mechanically dimple both sides of a specimen before chemically polishing or ion milling to obtain electron transparent thin area. Electropolishing allows better control than chemical polishing because the final thinning may be done in small increments by the use of a timer and relay to turn the electrical potential on for short intervals with the electrolyte flowing onto the specimen. However, this approach still requires frequent cleaning of the specimen, visual inspection at considerable magnification, and contributes to dirty foil surfaces. Some methods previously used were chemical polishing with a mixture of nitric, acetic, and hydrofluoric acids, [Holt, D. B. and Dangor, A. E., Philosophical Mag., Pg. 1921 (1963)], electropolishing with BK-1 electrolyte [described in Ultramicroscopy 9, (1982), pgs. 379-384 by the author], and

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by mechanical dimpling followed by ion milling. The desired specimens were to be used for crystalline to amorphous phase change studies in-situ in a TEM which required a damage free structure, ruling out thinning by ion milling. Chemical thinning was too rapid for good control of final thinning, required visual inspection after numerous thinning cycles, and often caused surface etching before rinsing could be done.

This work reports on improvements to an electropolishing technique that allow rapid production of clean germanium foils through automatic termination of the thinning process. The elimination of slow, tedious manual/visual final thinning is noteworthy.

Three problems solved during this experiment were, (1) uniform initiation of good polishing conditions on the surface of germanium, (2) development of a reproducible method for termination of the electropolish when the desired thin area was obtained, and (3) attainment of clean foil surfaces without surface damage in a reasonable period of time.

2. Equipment modification and calibration

A model 550-B jet thinning instrument, (South Bay Technology, Inc., 1120 via Callejon, San Clemente, CA 92672) was used for this work. This unit features a vertical, single jet, line-of-sight optical polishing termination configuration with excellent sensitivity, and a magnifier-equipped specimen viewing port to facilitate monitoring of the polishing process.

Modifications made were as follows. Standard quartz upper and lower light pipes in the jet head were replaced with sapphire pipes from the manufacturer. This eliminated changes in light pipe diameter due to attack by hydrofluoric acid which would decrease their light transmission efficiency. This change resulted in

excellent reproducibility of automatic shut-off of the polishing process when the desired thin area was obtained.

The "x" shaped plastic light pipe guide was coated on the edges of its four vane with silicone rubber adhesive. While the jet head assembly was positioned horizontally, the coated guide was gripped in small tweezers and slid along the light pipe toward the light source. The guide's final position was inside the PVC plastic jet support tube just above the nozzle threads. The adhesive was cured overnight at room temperature. When the guide was used in its normal position in the jet nozzle entrance, it partially obstructed the flow of the viscous electrolyte. This problem only occurred at the higher electrolyte flow required by the 3 mm size jet used for this experiment, but the new location of the guide was found to be convenient during cleaning and nozzle changing operations as well.

The standard infra-red LED light source was replaced with a visible red emitting LED. Its lower intensity allowed greater control of shut-off settings.

The following shut-off calibration procedure makes the light source intensity unimportant as long as it exceeds the minimum value required to trigger the shut-off detector when the specimen is adequately thinned. The 550-B control unit's front sensitivity knob, which adjusts the LED intensity, was set at 1.5. The detector bias knob at the rear of the unit was rotated to its least sensitive position. With no electrolyte in the jet unit, a microscope aperture disc containing a 150 micron hole was installed as a "test specimen" in the PVC specimen holder which was obtained with a platinum specimen contact from the manufacturer. The jet height was adjusted to 4 mm above the "test specimen". The control unit power was turned on, (with the voltage set at zero), and the auto polishing mode switch was reset. Next, the rear detector bias control knob was slowly rotated toward its maximum sensitivity setting until the light from the LED tripped the termination circuit off. This step was repeated to ensure a valid setting. The setting of the front sensitivity

control knob was rotated from the initial setting of 1.5 to a setting of 10 with the movable jet pivoted to the side of the "test specimen". When the shut-off trip circuit is reset, and the jet is rotated over the 150 micron test hole, the polishing circuit should switch off. The light intensity loss due to the electrolyte and absorption in the thin specimen was the reason for increasing the LED intensity setting from 1.5 to 10. The difference (8.5) was found to be the auto shut-off setting which resulted in either an electron transparent zone or a hole of about 20 microns in diameter with thin area around it. Changes in hole size or thin area merely required small plus or minus sensitivity knob setting changes around the initial setting of 10.

3. Electrolyte development

The initiation of a uniform dimple polish without preferential thinning at the edge of the dimple was sometimes difficult with BK-1 electrolyte regardless of whether a 1.5 mm or 3 mm nozzle hole size was used in a standard stainless steel jet.

The improved electrolyte, designated BK-3, eliminated this start-of-polish problem. It was prepared as follows. The primary solvent, 500 ml. of methanol, was cooled to -30°C in a polyethylene container while surrounded by dry ice and methanol in a secondary container. With constant stirring of the methanol, the following were slowly added; 50 ml hydrofluoric acid, 10 ml hydrochloric acid, 30 ml acetic acid, 1 ml bromine, and 90 ml of sulfuric acid which is very exothermic with methanol. The electrolyte temperature should not exceed 0°C . (A fume hood must be used for mixing and using this electrolyte.) Gloves made of nitrile material were found to resist these chemicals well, yet provided the necessary dexterity to operate the equipment.

The purpose of each electrolyte chemical is as follows. Methanol is compatible with the other ingredients below 20°C , provides good current density at a moderate

voltage, and it dissolves the reaction products of the polishing process well. Hydrofluoric acid and bromine dissolve the surface oxide and allow the polish to start uniformly across the dimple. Sulfuric acid provides sufficient ions to produce an adequate current density and polishing film thickness. This acid becomes rather viscous when cold and contributes to the electrolyte viscosity of 10.4 C.P. at -35°C which is ideal for use in the 550-B unit. No other chemical needs to be added to increase the solution's viscosity. Acetic acid aids the ability of the polishing film to uniformly polish across boundaries and dissimilar features, leaving them intact and well polished. Hydrochloric acid dissolves any germanium dioxide formed during the thinning process and reduced particulate surface contamination. The final solution composition was experimentally determined by changing the amount of the various ingredients mixed with a constant volume of 500 ml of methanol until the best results were obtained. The results are summarized in table 1.

The BK-3 electrolyte is moderately sensitive to temperature and viscosity changes which are inversely proportional to each other. When polishing was done at -40°C , the boundary in fig. 1 polished well but the matrix polished unevenly, due to the higher liquid viscosity at this temperature than at -35°C . When the electrolyte was deliberately used at -30°C to lower its viscosity, and a very slow electrolyte flow rate was used, the uneven polish seen in fig. 2 was the result. Inspection of this surface at 20,000 x in a scanning electron microscope revealed a grooved pattern similar to the TEM image. Therefore, an electrolyte temperature of -35°C and a moderate flow rate should be used.

4. Protection of polished surface

When using a single jet polishing apparatus, the process must be stopped about half way through the specimen. After cleaning, the dimpled surface referred to as the "side 1" dimple, must be coated with a material which transmits light yet is

resistant to attack by the electrolyte. The first coating tried, (which worked well on other materials) was red Microshield lacquer (Tolber Division, Pyramid Plastics, Inc., 220 W. 5th St., Hope, Arkansas 71801). Tolber is a subsidiary of Michigan Chrome and Chemical Co. When this lacquer was dissolved off the surface of germanium foils they looked clean and shiny optically but surface contamination that appeared "patchy" was seen in a TEM inspection. Apparently the electrolyte reacted with the lacquer to produce an insoluble residue.

A better protective coating for the "side 1" dimple was made by dissolving chips of Aremco Crystalbond Adhesive #509 (Aremco Products, Inc., P. O. Box 429, Ossining, New York 10562) in acetone in a small bottle. A small artist brush was used to apply this clear paint to the dimple. Since it was clear, the film thickness had little effect on the optical shut off reproducibility. Heat from a high intensity lamp placed above the specimen dried the coating to a slightly sticky surface in 10 minutes. The film was flexible rather than brittle, resisted chemical attack, dissolved in acetone, and did not stress the foil when "dry" like lacquer did.

5. Jet electropolishing procedure

Polycrystalline germanium discs with a purity of 7-9's, a diameter of 3 mm and a thickness of 0.3 mm were used for this work. They were lightly sanded on both surfaces with 4/0 emery paper before their rim was coated with Microshield lacquer, leaving an exposed area in the center about 1.8 mm in diameter. Microshield was used for this masking step due to its visible red color, easy removal with acetone, and lack of contact with the central dimple zone where it would cause surface contamination. The ability of this lacquer to dry completely in a few minutes also facilitated specimen handling.

The BK-3 electrolyte was added to a polyethylene jet polisher reservoir. The cooling tray around the reservoir was filled two thirds full with a mixture of 95% methanol and 5% water, then cooled to -35°C by the addition of chunks of dry ice.

While the electrolyte was cooling, the specimen was mounted on a specimen holder having a platinum contact ring to support the disc and provide good electrical contact during polishing. The disc was oriented with its partially masked surface facing upward, (toward the jet nozzle) and it was retained in place with a polyethylene diaphragm designed by the manufacturer for 2.3 mm specimens. Use of this hole size rather than the one used for 3 mm specimens plus the circumferential lacquer mask left a fairly small area exposed for polishing and prevented undercutting of the specimen rim during polishing. The loaded holder was then installed on the polishing unit.

Initial polishing with a 1.5 mm hole in a stainless steel jet produced polishing only at the edge of the exposed material. When a stainless steel jet with a 3.0 mm hole was used and a moderate liquid flow rate was established, polishing was still beginning only at the edge of the exposed region. With the jet set at 4.0 mm above the specimen, the following procedure was used to establish a good polish across the entire dimple. The electrolyte was pumped rapidly over the specimen through a 3.0 mm stainless steel jet to clear air bubbles from the system, then the flow was reduced to the slowest rate possible. The viscous fluid assumed the shape of a slender parabola with its apex just touching the specimen, yet flowing over it. The polishing voltage was ramped upward from 0 to 40 volts over a 5 second time period. The polish began at the dimple's edge and moved toward the center like a collapsing bullseye. After 30 to 60 seconds, the dimple was shiny and scratch free. While increasing the potential to 50 volts, the flow of electrolyte was simultaneously increased with visual monitoring to a steady stream rate at a pump setting of 50% to 60% of capacity. At a constant 50 volts, the observed current sometimes

decreased from 25 m.A. to 15 m.A., with no affect on the polishing quality. When the dimple depth appeared to be nearly half way through the specimen in about 3 minutes, the polisher power was manually turned off. The specimen was rinsed with methanol while still on the polisher. Then the holder with the disc was removed and rinsed in a beaker of methanol. Unloading was done using acid-resistant gloves made of nitrile. Finally the specimen was rinsed in distilled water, two acetone baths to remove the red lacquer, then two ethyl alcohol baths. While gripped across its diameter with a fine-pointed tweezers, the specimen was dried in a stream of room temperature air with a blower. Optical inspection of the dimple was done at 250x and 500x magnifications.

The specimen was then placed on a stereo microscope stage with the polished dimple facing upward. The dimple only was coated with the Aremco 509 "paint" previously discussed in section 4, and allowed to dry for 10 minutes. Next, the disc was inverted onto a piece of filter paper to prevent possible sticking to a glass slide, and its rim was coated with Microshield lacquer as described for the "side 1" masking described previously. When the lacquer was dry, the specimen was loaded in its holder and mounted on the polisher as before for the "side 1" polish. For "side 2", the same start up procedure was followed as that used for "side 1" of the specimen. In addition, the alarm buzzer was turned on that signaled when automatic shut-off of the polishing unit had occurred. The thinned specimen was gently rinsed with methanol, (the main electrolyte solvent) to prevent breakage of the thin area. There was no need to rush the rinse procedure for the following reason. A partially masked, shallow, electropolished dimple was exposed to the electrolyte flow with the voltage turned off. When the masking lacquer was removed, the germanium chemical removal rate determined by optical interference microscopy was only 1.7 nanometers per second, due in part to the cold electrolyte

temperature used. The finished foil was checked optically with both reflected and transmitted light at magnifications of 250x and 500x.

Foils obtained had either a hole of 20 to 30 microns in diameter surrounded by a thin region which revealed 2 or 3 interference fringes when viewed optically with reflected tungsten light as in fig. 3a, or a thin, unperforated region with interference fringes as shown in fig. 3b. Small changes in the front sensitivity knob setting were made to produce a majority of either perforated or thin, unperforated foils as needed.

Although one source of foil surface contamination was eliminated by changing the material used to coat polished dimples, some foils still had particulate surface contamination. The particles were thought to be the result of corrosion of the stainless steel jet by the electrolyte. These particles may have entered the electrolyte stream and deposited on the specimen where they resisted efforts to rinse them off.

To test this theory, a graphite nozzle, which was essentially inert to the electrolyte, was made in-house. A 3 mm hole was used because it had been found to be essential when starting to polish germanium. Two examples of clean foils made while using this special jet are shown in figs. 4 and 5.

6. Conclusions

This technique using BK-3 electrolyte and a slightly modified apparatus can be used to produce excellent TEM foils of polycrystalline germanium faster than with other methods. The concept of using an electrically conductive jet material that is chemically inert with respect to the electrolyte seemed to work well. Although a 3 mm jet hole is required, the process is consistent as long as proper procedures are followed. With practice, four or five good foils can be made per day including set-up and cleaning time. The skill and time formerly needed for manual/visual final

thinning in small increments are eliminated. In addition, damage free foils can be made more consistently than was previously possible. Continuous polishing until thin area was obtained also contributed to cleaner foils.

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Table 1
Effect of electrolyte content on the quality of polished foil surfaces

Initial Electrolyte	Chemical Added	Result Observed in TEM Examination
(1) 30 ml HF 90 ml H ₂ SO ₄ 1 ml bromine 500 ml methanol	(None)	Rough surface with some particles on it.
(2) 30 ml HF 90 ml H ₂ SO ₄ 1 ml bromine 500 ml. methanol	30 ml acetic acid	Smoother surface than (1) with particles on it.
(3) 30 ml HF 120 ml H ₂ SO ₄ 500 ml methanol	10 ml HCL 30 ml 2-butoxyethanol	Foil thickness slightly uneven but surface is smooth and clean.
(4) 30 ml HF 90 ml H ₂ SO ₄ 1 ml bromine 500 ml methanol	10 ml HCL	Slightly uneven foil thickness with a clean surface.
(5) 30 ml HF 90 ml H ₂ SO ₄ 1 ml bromine 500 ml methanol	10 ml HCL 30 ml acetic acid (graphite jet)	Smooth, clean surface. (A new S.S. jet left a few surface particles with this electrolyte.)

Figure Captions

- Fig. 1.** Excellent polish of a germanium boundary. Slight matrix irregularity is due to high electrolyte viscosity.
- Fig. 2.** Uneven surface polish on germanium caused by deliberately using a very slow electrolyte flow rate.
- Fig. 3A.** Hole in jet thinned germanium foil surrounded by interference fringes.
- Fig. 3B.** Thin, unperforated region in jet thinned germanium exhibits interference fringes and transmits 100 kV electrons.
- Fig. 4.** Clean specimen containing a boundary region, as thinned with a graphite jet.
- Fig. 5.** A dislocation retained in well polished, germanium thinned with a graphite jet.

Fig 1

500 nm

Fig. 2

Fig. 3

500 nm

500 nm

Fig 7

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