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Letter

Argon ion slicing (ArIS): a new tool to prepare super large TEM thin films from Earth and planetary materials

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Abstract: TEM foil preparation techniques commonly used in geology, material science and cosmochemistry are argon ion milling, ultramicrotomy and the Focused Ion Beam (FIB) technique. In this study we report on Argon Ion Slicing (ArIS), a new gentle preparation method which enables for the first time to prepare super large continuous and relatively smooth electron-transparent thin films (up to 50,000 μm^2) suitable for TEM use. So far Argon Ion Slicing was mainly applied on mono- or bi-mineralic samples in material science. We applied and improved this promising new technique on several geo-materials including two meteorite samples to prove the viability of ArIS on complex (polycrystalline, polyphase, porous) natural samples. The successfully obtained continuous electron-transparent thin films comprise an area of 44,000 μm^2 for Murchison (CM 2) and 30,000 μm^2 for the Allende (CV 3) meteorite samples, respectively. ArIS is a low-energy broad-ion-beam shadowing technique and benefits from an additional protection device (a copper belt). The sample portion directly beneath the belt is protected from the ion beam. The beam ''slices off'' the protruding sample parts on both sides of the belt and creates a large elongated wedge. Since the developing thin film is located almost parallel to the beam propagation direction, it is almost unaffected from any irradiation damage and a phase dependent preferred thinning is not observed. Rough sample edges were smoothened with a Cross section polisher prior to ArIS treatment, which turned out to be a crucial step to produce super large electron-transparent thin films.

Key-words: sample preparation, TEM, argon ion slicing, FIB.

1. Introduction

One obstacle to achieving the full potential of transmission electron microscopy (TEM) in Earth and Planetary Sciences is inefficient specimen preparation techniques. Many preparation methods and tools have been developed to produce thin films for TEM work, such as ultramicrotomy (Westphal *et al.*, 2004), electro polishing (Aebersold *et al.*, 1996; Kestel, 2000; Yao *et al.*, 2008), conventional argon ion milling (Barber *et al.*, 1970) and FIB (Heaney *et al.*, 2001; Wirth, 2004). Each of the mentioned techniques imparts a different sort of damage on the sample and therefore diminishes the maximum obtainable information a sample could yield. Every approach has pros and cons; ultramicrotomy requires impregnation of the sample in a wax or resin block which is cut in electron-transparent slices by a diamond knife after its solidification. Although a sample might lose all intrinsic information about structure details, and grains are often seriously distorted, it is still the means of choice when tiny unique particles (*e.g.*, cometary grains) are concerned, because no material is consumed during the preparation process (Westphal *et al.*, 2004). Another approach is to grind the specimen in an ethanol solution. Thereby obtained droplets are deposited onto a carbon coated grid. The sample can be used for nanoanalytical measurements after the solvent is evaporated. This extremely destructive process demands total sample consumption. Most information on structure, texture and the petrological context of a mineral assemblage is lost. In addition, the average thickness of grains enclosed in the drop can vary greatly – correlated with changing mineral hardness – which is extremely inconvenient for subsequent TEM analysis. According to Yao *et al.* (2008), electro polishing yields satisfying results when applied in material science. There, typical samples are mono- or bi-mineralic and homogenous with even surfaces (*e.g.*, semiconductors) and thus a gradient caused by any heterogeneity of the samples is not likely to be induced. A TEM disk (Ø = 3 mm) is mechanically polished to 150 μm thickness and is put into a solution with two acid electrolytes. An acceleration voltage is applied on two sides generating a strong electrolyte current which is accelerated towards the centre. There, the sample is mounted and etched and likewise polished into an electron transparent disk. The acid treatment is applied on metals and semiconductors. The inevitable surface amorphisation

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destroys any intrinsic crystallographic information of crystalline sample material which is present prior to the procedure. Barber (1970) and Barna *et al*. (1999) report on argon ion milling also referred to as ion etching. This technique employs a broad argon ion beam to thin samples to electron transparency. The beam hits the surface at a low incident angle. It is deflected several times toward the sample surface if a grid is mounted on its top; after a certain time holes open up during the continuous ion bombardment. A small sample area (typically a few square micrometres) surrounding each hole turns electron transparent but this area rapidly becomes thicker moving away from the hole. Thus, only the tips of the created wedges are electron transparent. Heterogeneous, polycrystalline and polyphase rocks often result in unevenly thinned TEM specimens since the mineral hardness influences the abrasion efficiency of the ion beam. Likewise, different orientations in monomineralic rocks have a strong influence on the resulting surface morphology. All above mentioned techniques cause significant sample loss or sample destruction. Only recently focused ion beam milling (FIB) became available which enabled precise site specific thinning for the first time (Heaney *et al*., 2001; Wirth, 2004; Scott *et al*., 2006). Here a focused heavy ion beam (*e.g.*, Ga^+) is used to cut out a slice of a precisely defined site of interest from a thin section or out of a polished bulk specimen, leaving the remaining sample more or less unaffected. Electron-transparent areas obtained by FIB are typically $\leq$200 μm^2. Drawbacks of this technique are the expensive equipment and the time consuming procedure. The Ga^+ ions cut approximately 15 × 10 μm or 10 × 20 μm into the sample along a prior deposited Pt strap. This strap prevents charge effects on the sample surface (which would otherwise deflect the ion beam and hamper precise milling) and protects the underlying sample surface from irradiation. The obtained TEM specimen is located perpendicular to the sample surface. The incident beam hits the surface of the specimen at a right angle. Before the technique was improved by invention of the dual beam FIB mode (Giannuzzi *et al*., 2007), rather surface-related features were easily destroyed if a 80–100 nm thin gold film was not deposited beneath the Pt strap (Lee, 2007). Before, the Ga^+ beam was used for both cutting and monitoring. But the high-energy beam can amorphise, resp. destroy features close to the surface while being used for scanning the sample. Dual beam machines utilize two beams, an electron beam for monitoring and a high energy (30 kV) Ga^+ beam for the cutting procedure. This modification helps to preserve sensitive crystalline material on the surface. ArIS was only recently applied on a sample recovered from a diamond anvil cell (DAC) high-pressure experiment by Tateno *et al*. (2009). Tateno *et al*. (2009) attach the DAC sample onto a Si wafer (2.8 × 0.5 × 0.5 mm) with a polymeric resin. This assemblage is thinned to a total thickness of 100 μm with sandpaper before it is glued onto the ArIS sample holder. The sample is treated in two intervals, one at $0°-0.5°$, a very low angle, and at an acceleration voltage of 6.5 kV for 2 h. The other is conducted at an incident angle of $3.0°-5.0°$ and an acceleration voltage of 4.0 kV for 1 h. Prior to the second interval the sample block is placed upside down, the second milling thus aims at the opposite side of the sample. The resulting electron-transparent area (thinner than about 100 nm) did not exceed 200 μm^2. Another attempt yielded approximately 500 μm^2.

We developed a new preparation strategy and employed ArIS under completely different operating conditions and report here on electron-transparent areas exceeding 40,000 μm^2 of a continuous thin film, which is an improvement of several orders of magnitude.

2. Methods

2.1. Mandatory sample pre-treatment

A petrographic thin section has to be prepared, ideally with a sample thickness of 100 μm. The use of removable glue is highly recommended, though not mandatory. Small rectangles (2 × 3 mm) are drilled into the sample material down to the glass slide using an ultrasonic drill (Fig. 1a–e). Circular TEM grids are cut in half before being glued onto the rectangle surfaces with a 2-component glue. The small sample rectangles are removed from the slide with acetone. After drying, they are mounted into a JEOL SM – 09010 Cross Section Polisher to fine polish their edges which are more or less corrugated by the drill-out procedure. The edge-polishing treatment of the sample is crucial for the quality and therefore the maximum size of the electron-transparent area obtained during the subsequent ArIS treatment. We assembled clamps (Fig. 2) on both sides of the ArIS sample holder to omit gluing the sample onto the holder as originally intended by JEOL.

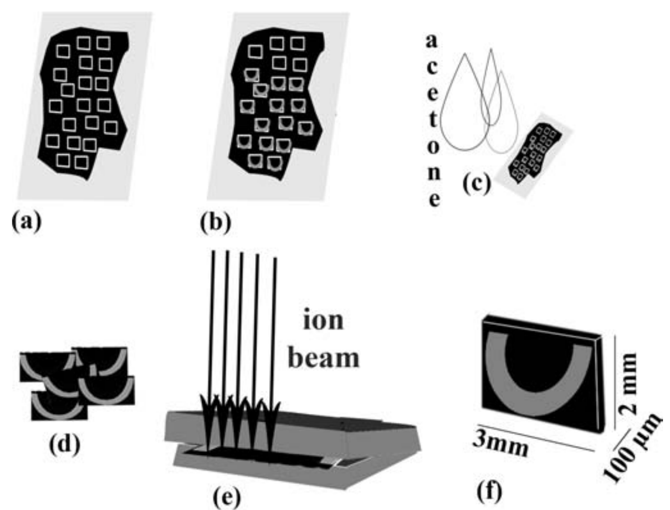

Fig. 1. Schematic pre-treatment steps: thin section (a) with drilled rectangles, (b) with attached TEM grids; (c) acetone treatment separates samples from glass slide; (d) separated samples; (e) cross section polish treatment smoothens sample edges; (f) sample ready for ArIS treatment.

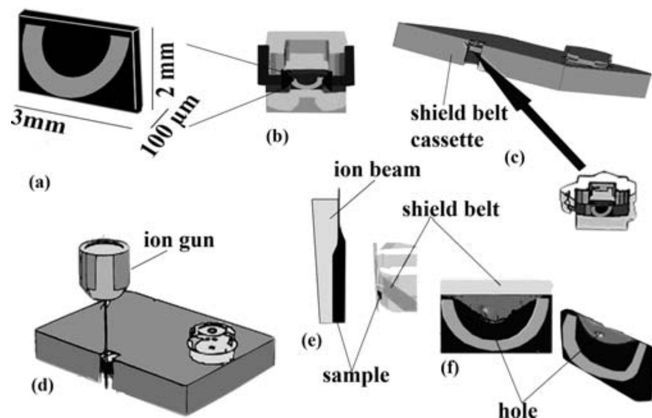

Fig. 2. Schematic ArIS process steps: (a) pretreated sample ready for ArIS; (b) sample holder; (c) orientation of sample holder in shield belt cassette; (d) ion gun is aligned parallel to sample and shield belt; (e, left) beam/sample orientation side view; (e, right) sample holder, sample and shield belt side view; (f) sample with lagoon shaped deepening, the rim thickness tapers to only a few nanometres towards the hole in the lower region of the deepening.

2.2. JEOL EM-09100IS argon ion slicer

Similar to conventional argon ion milling, ArIS produces a wedge of which the tip is electron transparent. Contrary to argon milling a wedge produced by ArIS and particularly its tip is elongated over several 100 µm. ArIS utilizes a broad ion beam. A copper belt located precisely above the narrow edge (30–100 µm thick) of the sample shields a lamellar sample portion from the beam. This portion remains almost unaffected by irradiation under the protection device. Steps of the process are illustrated in detail in Fig. 2. The wedge is created by letting the incident beam hit the protruding sample parts almost at a right angle. The copper belt itself deflects the beam slightly contributing to the before mentioned inclination of the incident beam, which alternates between front and backside during the slicing procedure. The inclination of the incident angle can be varied from parallel (0°) to 6° with respect to the plane of the sample surface and Cu-belt. An acceleration voltage between 0.5 and 8 kV can be applied. The entire sample stage is rocked from side to side while the slicing is in process, this would reduce the effect of preferential slicing. A camera located in the slicing chamber enables ''*in situ*'' observation during the thinning procedure. This is extremely important because treatment times can vary greatly depending on sample thickness and material properties and the slicing process has to be interrupted by the operator manually. The procedure is usually interrupted when the first small hole starts to open up in the sample.

The subsequent TEM investigation requires thin carbon coating. For this the whole assemblage (sample together with the sample holder) is mounted into a carbon coating machine. After the coating procedure the sample is ready for analytical study.

3. Natural test-samples

3.1. Murchison

Out of a small bulk specimen a thin section of approximately 100 µm thickness was prepared in our lab. We recovered three rectangles (2 × 3 mm), two with intact and one with a strongly corrugated edge by using an ultrasonic drill. Each edge was treated approximately 230 min with a JEOL SM-09010 Cross Section Polisher. After attaching half TEM grids onto the sample surfaces and removing the glass slide with acetone, one Murchison sample was mounted into the ArIS sample holder and the slicing was conducted at 4.5 kV and ~18 µA at an incident angle of 1.5°. The total processing time was 276 min. The process was interrupted after the first holes started to open up.

3.2. Allende

The specimen was on hand as an ultra fine polished thin section of approximately 30 µm thickness. We cut out seven intact (2 × 3 mm) and two corrugated rectangles using an ultrasonic drill. After having attached half TEM support rings onto the rectangles, they were removed from their glass slides with acetone. Subsequently each was treated approximately 230 min with a JEOL SM-09010 Cross Section Polisher. The edges were smoothened at 4.5 kV and an argon flux of approximately 2.5 sccm. Allende was mounted onto the ArIS specimen holder and treated in subsequent intervals which summed up to 193 min in total. The sample was treated at 4.5 kV and ~18 µA at an incident angle of 1.5° and an argon flux of 7.7 sccm.

4. Results

We obtained a 44,000 µm^2 large thin film from Murchison which is documented in Fig. 3 and a 30,000 µm^2 large electron-transparent area from Allende, documented in

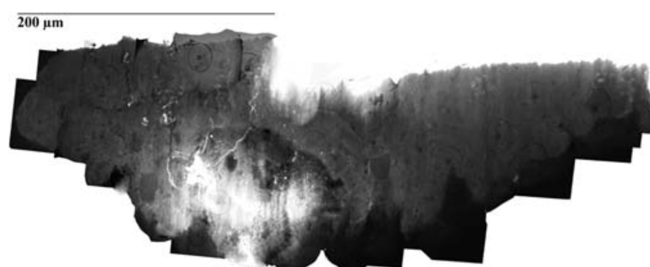

Fig. 3. Bright-field (BF) TEM images document the large continuous electron transparent area obtained from Murchison. The outer rims are slightly thicker than the area in the centre surrounding the holes (light area) [thickness ranges from 0 (hole) to 120 nm (outer rim)]. The thickness difference is not large and the entire area documented is accessible to TEM investigation.

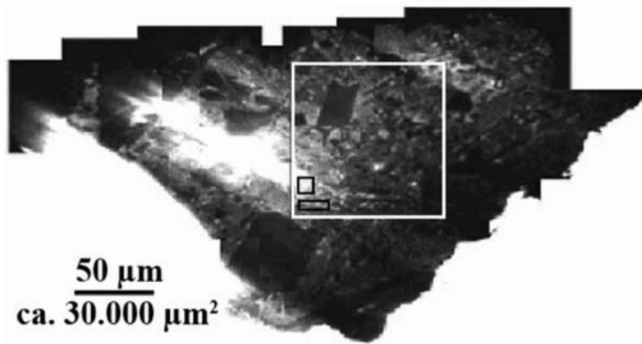

Fig. 4. BF TEM stitched screen shots of Allende; small black square is area typically used for NanoSIMS measurements (10 × 10 µm); little black rectangle below is area typically obtained from FIB; large white square is 100 × 100 µm.

Fig. 4. We had to take screen shots from the fluorescent screen of the microscope to document the entire electron-transparent area. The resolution of the assembled CCD camera is too high and the lowest resolution still offering enough contrast to observe material details produced images with 13 × 13 µm side length (196 μm^2).

5. Discussion

We started the refinement of the slicing procedure by applying ArIS on homogeneous synthetically produced monomineralic samples (amorphous SiO_2 and a single crystal enstatite). This approach seemed to be the best way to extinguish machine-induced artefacts and to enlarge the produced TEM foil. We produced electron-transparent areas which were not exceeding 1000 μm^2. Furthermore, the electron-transparent area was comprised of randomly distributed small thin foil patches. Unlike Tateno *et al*. (2009), we conducted our treatment at constantly low incident angles and low acceleration voltages, making a later surface treatment (to remove the amorphised surface layer) unnecessary. Gluing the sample onto the holder with wax, as recommended by JEOL, poses an unnecessary risk to damage the sample during the demounting step. The sample holder + sample would have to be reheated after the thinning to re-liquefy the wax. This implies that one would have to pull and push the sample gently to loosen it from the holder. Therefore, two clamps were assembled to each side of the specimen holder which stabilize the sample in its position on the holder. The ultrasonic drill, which we use to cut out the rectangles out of a thin section, was believed to be gentle enough to produce good starting material for the subsequent treatment. Good in this case means even enough sample edges. This is necessary since the sample edge has to be placed neatly under the protection device across its entire length. A zigzag or undulating edge has got a changing ''sample to belt'' distance. From our attempts with monomineralic material we learned that even only gently corrugated edges generate strong surface patterns (stripes and ripples with random distances) which are extremely inconvenient for later TEM work. These patterns seemed to be linked directly to the undulating sample edge. Furthermore, this edge gave rise to serious beam deflection and diminished the size of the later obtained electron transparent thin foil to only a few hundreds of square micrometres. Beam deflection is inevitable when it hits an uneven sample edge. We concluded that a rectangle with perfectly smoothened edges would not show any surface oddities and would develop a substantially larger electron transparent area; we therefore decided to additionally smooth the edges with a JEOL Cross section polisher. The results were large thin areas (thinner than 1 µm) covering an area of 500 × 500 μm^2 with embedded super large continuous electron-transparent areas of ten thousands of square micrometres (Allende 30,000 μm^2 and Murchison 44,000 μm^2). The obtained areas of course are thinner around the hole but do not exhibit a strong thickness gradient which might hamper subsequent analytical treatments strongly (HRTEM might not be possible from thicker outer rim regions). ArIS produces a lagoon shaped deepening (Fig. 2f) typically with a length of 500 µm across the sample edge and tapering off further down along the sample surface. Thick sample parts remaining around this thinner lagoon are stabilizing the sample extremely, making it insensitive to transport or mounting and demounting into different holders. Likewise, the prior attached copper ring yields additional stability. Regardless of the composition of the treated material, 4.5 kV and an incident angle of 1.5° proved to be ideal operating conditions. The development of a lagoon shaped deepening (Fig. 2f) is extremely important. Under ideal operating conditions the resulting wedge (Fig. 2e) reaches its maximum size and its tip, which resembles the electron-transparent area, is elongated to a maximum. We did not observe mineral phase dependent abrasion thus ''soft'' matrix material is located next to hard crystalline material in both Allende and Murchison. Due to the low acceleration voltage and the unique incident angle, the later observed thin film shows neither amorphisation nor any other irradiation damage. Both meteorite samples were chosen to prove the viability of ArIS on complex, polycrystalline, polyphase, porous natural samples. ArIS proved its capacity of producing super large TEM foils. The application of ArIS is obviously not restricted to planetary sciences and cosmochemistry, though it will certainly complement data which were obtained by FIB or argon ion milling. It will be of benefit in every research field where small micro- or nano-sized features are investigated, such as structural geology and experimental mineralogy. The preparation of ArIS samples ready for TEM work does not exceed 9 hours, which includes all steps from cutting the specimen rectangle out of the thin section to mounting the specimen into the TEM holder. In upcoming projects we intend to apply several nano-analytical techniques on the same ArIS treated samples, *i.e.* NanoSIMS, TEM and Synchrotron–XRF.

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