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Parallel preparation of plan-view transmission electron microscopy specimens by vapor-phase etching with integrated etch stops

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ABSTRACT

Specimen preparation remains a practical challenge in transmission electron microscopy and frequently limits the quality of structural and chemical characterization data obtained. Prevailing methods for thinning of specimens to electron transparency are serial in nature, time consuming, and prone to producing artifacts and specimen failure. This work presents an alternative method for the preparation of plan-view specimens using isotropic vapor-phase etching with integrated etch stops. An ultrathin amorphous etch-stop layer simultaneously serves as an electron transparent support membrane whose thickness is defined by a controlled growth process such as atomic layer deposition with sub-nanometer precision. This approach eliminates the need for mechanical polishing or ion milling to achieve electron transparency, and reduces the occurrence of preparation induced artifacts. Furthermore, multiple specimens from a plurality of samples can be thinned in parallel due to high selectivity of the vapor-phase etching process. These features enable dramatic reductions in preparation time and cost without sacrificing specimen quality and provide advantages over wet etching techniques. Finally, we demonstrate a platform for high-throughput transmission electron microscopy of plan-view specimens by combining the parallel preparation capabilities of vapor-phase etching with wafer-scale micro- and nanofabrication.

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1. Introduction

Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) in a plan-view orientation are widely used in the research and development of nanostructures, nanoparticles, and thin films. By orienting a specimen surface perpendicular to an electron beam, plan-view analysis provides direct observation of in-plane and interfacial phenomena including nucleation, morphology, defects, strain, and catalysis. However, while advancements in monochromation [1], aberration correction [2–5], detectors [6,7], and high energy resolution spectrometers [8,9] have ushered in new TEM resolution limits and analytical capabilities [10–12], sample preparation remains a critical and often limiting factor in determining the quality of characterization data obtained.

Conventional methods for preparing self-supporting plan-view specimens rely upon iterative physical and/or chemical etching performed in a serial fashion [13,14]. There is no inherent protection against removing too much material which can rapidly damage or destroy a specimen. However, removing too little material results in an excessively thick specimen and leads to image blurring due to increased chromatic aberration effects. There remains a need for alternative preparation methods that are high-throughput, produce mechanically robust specimens, and achieve optimally thin plan-view specimen geometries while minimizing preparation induced artifacts.

1.1. Background

Physical etching is widely used to prepare bulk specimens for electron microscopy by mechanical grinding, polishing, dimpling, Ar-ion milling, and focused ion beam (FIB) milling [15]. In practice, physical etching is commonly performed in a blind and iterative fashion, requiring frequent optical inspection to ensure that the desired specimen thickness, typically ≤100 nm, is obtained. While physical etching by hand provides limited site specificity, dual-beam FIB instruments are well suited for preparing site-specific specimens. However, FIB preparation requires significant upfront capital investment, operating costs, and is less readily suited to plan-view preparation, although methods had been developed [16,17]. Furthermore, both hand and FIB preparation methods are reported to take between 2 and 6 h to produce a single high quality specimen, even when performed by an experienced microscopist [14,17]. Physical etching processes may also damage and

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amorphize a specimen during preparation causing significant changes in physical and chemical properties [16,18].

Plan-view specimen preparation by chemical etching has also been demonstrated using backside wet etching of silicon [19–21]. A typical configuration consists of a silicon substrate with a SiO_2 support membrane formed by thermal oxidation. Following deposition of the material of interest onto the SiO_2 layer, a cavity is wet etched into the substrate from the backside, producing an electron transparent window through the now freestanding SiO_2 layer. However, several practical challenges arise when implementing such protocols. First, wet chemical etching requires the preparation, use, and disposal of hazardous liquid chemicals. For example, $HF:HNO_3$ in a 1:1 concentration is commonly used for rapid Si substrate etching, while tetramethylammonium hydroxide (TMAH) heated to 70 °C has been used to increase the etch selectivity of Si against SiO_2 in the final thinning process [20]. To minimize the microscopist's exposure to chemicals, an optical microscope is commonly positioned near the sash of a fume hood with active ventilation [21]. However, the toxicity of both HF and TMAH remains of great concern because the microscopist must operate in close proximity to the wet etchants and their vapor in order to monitor the specimen throughout the etching process. Second, due to limited etch selectivity and timing constraints, specimen thickness is difficult to control making specimen-to-specimen repeatability difficult to achieve.

An alternative to both chemical and mechanical thinning is to eliminate the need for thinning entirely by direct deposition onto a grid with a prefabricated support membrane or porous network. While convenient, commercially available prefabricated support grids are not always suitable or desirable for practical reasons. First, in the case of conformal deposition techniques such as chemical vapor deposition (CVD) and its variants including metalorganic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD), grids with support membranes are often unsuitable due to deposition onto both frontside and backside faces by vapor-phase precursors. To prevent deposition onto both membrane faces, mechanical masking structures have been developed [22,23]. However, these solutions are not always viable due to their limited temperature stability and introduction of contamination into deposition environments. Second, standard 3 mm diameter grids are incompatible with automated wafer handling equipment designed for processing wafers with standard dimensions. This restricts their utility in semiconductor process development and monitoring applications where automated wafer handling and load-lock transfers are commonly used. Third, the use of 3 mm commercially available TEM grids can alter growth kinetics and deposition conditions which are highly sensitive to surface topology, areal loading, as well as substrate thermal mass and transient behavior. To truly study "representative" materials in their as-grown conditions, it is desirable to obtain a specimen from an in-process substrate thereby ensuring that the final TEM specimen experiences identical fabrication conditions.

With these objectives in mind, we present a method for preparing plan-view specimens using isotropic vapor-phase chemical etching with integrated amorphous etch stops. We demonstrate how this approach can be scaled to batch (parallel) preparation of multiple specimens from a plurality of samples to enable high-throughput electron microscopy studies. The use of an etch-stop layer enables precise and uniformly thin (< 10 nm) specimen geometries to be realized. Finally, we demonstrate the integration of parallel preparation with wafer-scale processing, enabling TEM/STEM analysis of layers, test structures, and functional devices formed using conventional micro- and nanofabrication techniques.

2. Methods

Fig. 1 presents a schematic outline of the vapor-phase preparation process. Fig. 1(a) shows an exploded view of a prototypical sample cored to form a standard 3 mm diameter specimen. In the baseline process, the substrate is composed of a standard silicon wafer or piece (200–550 μm thick) with a thermally grown SiO_2 layer. The selection of these commonly available materials and processes allows for the greatest compatibility with standard lab equipment and materials. If a TEM specimen holder cannot accommodate the full substrate thickness, a coarse (≥ 30 μm) polishing paper can be used to reduce the substrate from the backside to a suitable thickness. To accommodate a wide range of holders while retaining mechanical robustness, we target a substrate thickness of 200 μm. A SiO_2 sacrificial layer with thickness ≥300 nm is included to provide electrical isolation between the layer of interest and the silicon substrate. This allows the top

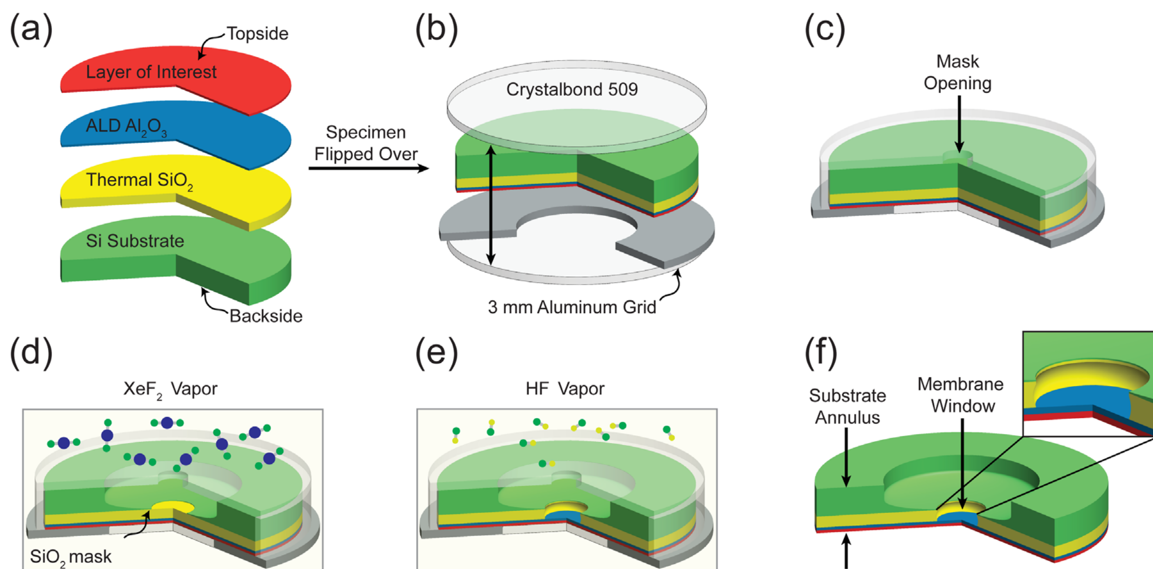

Fig. 1. Schematic of specimen preparation process (not to scale): (a) exploded view of layered geometry, (b) mounting and protection of the specimen for preparation, (c) opening of backside mask exposing the silicon substrate, (d) vapor-phase xenon difluoride silicon etch, (e) vapor-phase hydrofluoric acid SiO_2 etch, and (f) final specimen after removal of the protective barrier layer.

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