Si-integrated ultrathin films of phase-pure \(^{3}\text{Y}_{3}\text{Fe}_{5}\text{O}_{12}\) (YIG) via novel two-step rapid thermal anneal

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\textbf{ABSTRACT}

Traditional one-step annealing of ultrathin amorphous Y–Fe–O films on Si has been reported to yield ‘incomplete crystallization’. Here, it is shown that films produced by standard anneals (e.g.: 800°C, 3 min) actually contain yttrium iron garnet (YIG) crystallites in a nanocrystalline non-garnet matrix. During \textit{in situ} TEM laser annealing, a low-temperature pre-anneal enabled subsequent YIG crystallization at velocities of 280 nm/s that prevented the formation of the nanocrystalline matrix. From these results, a two-step rapid thermal anneal was identified (400°C, 3 min; 800°C, 3 min) that successfully produces phase-pure garnet films on SiO\textsubscript{2} on Si.

\textbf{IMPRINT STATEMENT}

A novel two-step anneal discovered through \textit{in situ} TEM laser annealing produces phase-pure, fully crystallized ultrathin YIG films grown on SiO\textsubscript{2} on Si.

\textbf{Introduction}

Recently, the insulating nature and low-magnon damping coefficients of yttrium iron garnet (YIG) have moved this material to the forefront of research in spintronics. For example, low damping coefficients lead to long magnon lifetimes that are critical for spin logic and spin current generators [1–12]. Current research uses either bulk YIG (polycrystalline, 3–10 \(\mu\)m grains) [13] or epitaxial YIG (on gadolinium gallium garnet) [14–17]. These forms of YIG are expensive, non-abundant, and not ideal for integration with other system components, such as semiconductor electronics and lasers. In addition, proximity-based spin-pumping effects diminish inversely with the thickness of the YIG proximity layer so ultrathin YIG is desired but difficult to integrate with Si [18]. Fortunately, the photonics community has been improving the growth of ultrathin YIG onto semiconductor-compatible substrates for on-chip optical isolators [15,19–23].

The most promising method for integration of YIG thin films onto non-garnet substrates has been to simply anneal amorphous films made by sputter or pulsed laser deposition [14–15,20,24–29]. High temperatures are required to achieve the garnet phase, and a number of other phases can form with large strains due to thermal expansion mismatch [24,30]. Secondary phases inhibit the formation of garnet and severely hinder device performance. Despite these challenges, polycrystalline YIG has been grown on non-garnet substrates with varying degrees of success [24,26–27,29–32]. Thinner films have proven to be exceptionally challenging [24]. X-ray diffraction (XRD) is typically used to demonstrate the presence of the garnet phase and to rule out the presence of other phases. Yet, when subsequent devices
underperform, incomplete crystallization is usually identified as the cause [20,33]. This indicates that XRD alone is not sufficient to study the growth mechanisms, microstructure, or true phase purity of the films.

In this paper, we use conventional, in situ, and time-resolved transmission electron microscopy (TEM) to study the amorphous-to-crystalline phase transition for YIG films grown on SiO2 on Si. First, the microstructures and nanostructures produced by common annealing conditions were investigated using conventional TEM. The diffraction patterns of the films indicated phase-pure YIG despite the obvious presence of a nanocrystalline matrix in the bright-field images. Second, in situ laser annealing was used to study the nucleation and growth of YIG crystals. These experiments sparked the idea for a novel ex situ two-step anneal. Specifically, low temperatures were shown to produce YIG crystallites that grew rapidly under subsequent standard annealing temperatures to produce large crystals of YIG. Finally, phase-pure YIG thin films were successfully grown on SiO2 on Si by technologically viable RF reactive sputter deposition followed by our newly discovered two-step rapid thermal anneal (RTA).

**Methods**

YIG thin films were deposited at room temperature onto SiO2 TEM grids (TEMWINDOWS, 40 nm) using RF reactive sputter deposition. A Y:Fe (3:5) metallic target was sputtered with forward powers of 240 W and Ar:O2 gas flow ratios of 20 sccm:2 sccm. Deposition rates of 2.5 nm/min yielded films from 10 to 130 nm thick as measured by X-ray reflectivity using the Si wafer onto which the TEM discs had been placed during deposition.

Initial films were annealed in N2 at atmospheric pressure by standard RTA (800°C, 3 min). As-deposited and annealed films were analyzed with an FEI Tecnai Femto TEM operated in thermionic mode at 200 kV. This microscope also enabled in situ laser annealing with a Light Conversion Pharos Yb:KGW laser (343 nm, 20–90 mW). The laser was operated at a repetition rate of 25 kHz during annealing. The full-width at half-maximum (FWHM) of the laser spot was 138 μm.

To test the in situ laser-prompted discovery of two-step annealing for full YIG crystallization, subsequent films were annealed in N2 at atmospheric pressure by RTA for varying times and temperatures, including 800°C, 400°C, and 400°C followed by 800°C. All anneals were conducted for 3 min at each temperature.

Magnetic characterization of the YIG films was performed using an alternating gradient magnetometer (AGM) (MicroMag 2900, Princeton Measurement Corporation) where the field was swept ±10 kOe and measured at 100 Oe increments with a sampling frequency of 5 data points per second.

**Results and discussion**

**Standard rapid thermal annealing**

To benchmark typical microstructures and nanostructures, YIG films were deposited on TEM grids with SiO2 windows and imaged before and after standard annealing (RTA at 800°C for 3 min), shown in Figure 1(a,b, respectively). Figure 1(a) verifies that films were amorphous as-deposited. There were no structural features in the bright-field images, and the diffraction patterns were single diffuse rings due to a regularity in interatomic spacing typical in glassy structures [34]. After annealing, Figure 1(b), the microstructure was similar to that typically seen in integrated YIG films by dark-field optical microscopy and scanning electron microscopy/electron backscatter diffraction [24]. Micrometer-sized crystallites (1–2 μm) were observed in a seemingly amorphous...
matrix. These crystallites contained the desired garnet phase, but they only accounted for 80% of the sample area. However, because the YIG regions were highly crystalline, they were strongly diffracting and accounted for almost all of the intensity in the diffraction pattern, Figure 1(c). The angular intensity of the diffraction pattern was uniform, suggesting that the crystallites had no preferred in-plane texturing. The characteristic dark streaks throughout the crystallites arise from bend contours, a common diffraction-contrast feature in single-crystal films.

Further analysis of the matrix phase indicated that it was nanocrystalline (5–20 nm grains) rather than amorphous. Figure 2(a,b) shows bright-field images of this region with speckled contrast, which is indicative of multiple grains. Selected-area diffraction patterns (SADPs) of the matrix confirmed the presence of a crystalline phase. SADPs obtained at normal incidence consisted of sharp, continuous rings, signifying no in-plane texturing was present, Figure 2(c). However, tilting the specimen revealed a strong out-of-plane texturing in this nanocrystalline phase, as shown in Figure 2(d). Though the small grain size led to peak broadening, radial integration of the SADP, Figure 2(e), indicated that the matrix posed of out-of-plane textured \( \text{Y}_2\text{Fe}_4\text{O}_9 \) nanocrystals. Due to the texturing, the relative peak intensities differ from those arising from a non-textured film, as can be seen by comparison to a simulated \( \text{Y}_2\text{Fe}_4\text{O}_9 \) pattern. Importantly, the \( \text{Y}_2\text{Fe}_4\text{O}_9 \) phase does not have desired ferromagnetic or magneto-optical properties, which explains the reduced performance in YIG films reported in the literature after standard RTA annealing \cite{16–17,21–25,33}.

**In situ TEM laser-induced crystallization**

In order to study the amorphous-to-crystalline phase transition for YIG, in situ TEM laser-annealing studies were conducted on films deposited onto SiO\(_2\) on Si. These were similar to the as-deposited films shown in Figure 1(a). A relatively high average laser power (82.6 mW; 1 s; Gaussian shape) was used for in situ crystallization of the amorphous film. Further irradiation with this power produced no additional changes in the structure. Three regions with different crystallization behavior were identified, the formation of which is attributed to differences in temperature caused by the Gaussian energy profile of the laser similar to other in situ laser annealing studies, Figure 3(a) \cite{35–36}. The central dark region (red) was a nanocrystalline phase and was highly textured in-plane radially from the center of the spot due to the direction of thermal transport (see Supplemental Information). The second region (yellow) is shown more closely in Figure 3(b,c). The large grains in this region show bend contours due to the highly ordered crystalline structure, similar to the YIG crystallites in the RTA-annealed sample above. This region was pure YIG, as verified with SADP (inset of Figure 3(c)). The third region (blue), along the outer regions of the laser spot, was comprised of YIG crystallites that appeared to have seeded the growth in the second region. Using
the known FWHM of the laser intensity, and assuming the second region reached the crystallization temperature of YIG (800°C), the third region was estimated to have reached 400°C (see Supplemental Information).

This growth behavior was unexpected, and it suggested that a low-temperature anneal could produce nuclei and/or seed crystallites, thereby enabling the rapid formation of YIG during subsequent high-temperature anneals. This low thermal budget concept for obtaining fully crystallized films is very appealing for eventual use in high-quality spintronics and photonics devices.

To study this idea further, a lower average power of 25.2 mW was used to form crystallites in as-deposited films, Figure 3(d). Further laser irradiation at this power did not produce any additional structural changes. However, increasing the average laser power to 32.0 mW caused these crystallites to grow with a crystallization front velocity of 280 nm/s, determined using time-resolved TEM, see Supplemental Information. Although the laser profile again yielded different behavior for the outer region of the beam, the entire center of the laser-annealed area was phase-pure YIG after this two-step anneal, Figure 3(e).

**Novel two-step rapid thermal annealing**

This study was brought full circle by applying the newly discovered means of nucleation and growth to a two-step RTA, which can be up-scaled for use with spintronics and photonics devices. YIG films (25 nm and 130 nm thick) were annealed by either standard RTA (800°C, 3 min), low-temperature RTA (400°C, 3 min), or two-step RTA (400°C, 3 min; 800°C, 3 min). The first RTA process has been the most common anneal for YIG \([17,20,24,26–27,29–30,37]\) since its discovery \([30]\).

Magnetic hysteresis measurements (Figure 4) were used to determine the extent of crystallization for YIG films that were annealed using both the standard RTA and the two-step RTA. The films produced by standard RTA had saturation magnetizations of 99.6 emu/cc, which is 27% lower than expected for pure YIG. Significantly, the YIG films annealed by the new two-step RTA had saturation magnetizations of 130.6 emu/cc, which is within experimental error (e.g.:
Figure 4. Out-of-plane hysteresis loops of 130 nm thick YIG films annealed using standard RTA (800°C, 3 min) and the new two-step RTA (400°C, 3 min; 800°C, 3 min).

film volume measurements) of reported values for YIG of 136.7 emu/cc [38]. These results are in fair agreement with the difference in the garnet versus nanocrystalline areas found in the bright-field images shown in Figure 1.

Additional TEM characterization supported the AGM result that the novel two-step RTA produced completely crystallized (phase-pure) YIG films, Figure 5(a), rather than the typical crystallites in a nanocrystalline matrix, which are produced by standard RTA, Figure 5(b).

The diffraction patterns in Figure 5(c) underscore the challenge associated with determining the phase purity of YIG films from diffraction alone. Both patterns, corresponding to images on the left, have similar peak intensities and highly consistent peak locations. These patterns strongly suggest that standard, large-area Bragg–Brentano diffraction patterns (XRD) are not sufficient for reporting YIG crystallization of integrated devices because amorphous and ‘x-ray amorphous’ (nanocrystalline) phases will not appear in these patterns.

In summary, the serendipitous discovery of a two-temperature anneal to aid the crystallization of YIG from thin films of amorphous Y–Fe–O led to the integration of phase-pure YIG films onto SiO₂ on Si substrates. YIG films using standard single-temperature anneals are known to have poor performance in photonics even when standard diffraction patterns exhibit only garnet peaks. This has been attributed to incomplete crystallization [20,33]. Here, TEM analysis has shown that this matrix is actually a nanocrystalline, non-garnet phase accounting for over 20% of the sample. Due to the small grain size, this nanophase does not appear in the large-area diffraction pattern of YIG films, making it difficult to detect by standard characterization methods. In studying the crystallization of films using in situ laser annealing, seeding of garnet crystals was observed from crystallites.

Figure 5. Bright-field TEM images of 25 nm YIG films (a) annealed at 400°C for 3 min and subsequently annealed at 800°C for 3 min and (b) annealed at only 800°C 3 min. (c) Radial integration of diffraction patterns for films annealed at various conditions. The diffraction patterns appear similar, but unlike standard anneals, the two-step anneal successfully produced phase-pure YIG.
produced at relatively low temperatures. Propagation of the crystallization front (280 nm/s) of garnet allowed this phase to consume the amorphous regions before the nanocrystalline phase could form. A commercially feasible two-step RTA technique (400°C, 3 min; 800°C, 3 min) was then proposed and successfully used for complete crystallization of phase-pure YIG films on SiO2 on Si. In addition to YIG, this innovation may be applicable to the Si-integration of other technologically important oxides, such as yttrium aluminum oxide (YAG) [39], and it will most certainly play an important role in future device research and applications in nonreciprocal photonics, spintronics, and topological insulators.

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