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Human-AI collaborative autonomous synthesis with pulsed laser deposition for remote epitaxy

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ABSTRACT

Autonomous laboratories typically rely on data-driven decision-making, occasionally with human-in-the-loop oversight to inject domain expertise¹⁻⁶. Fully leveraging AI agents, however, requires tightly coupled, collaborative workflows spanning hypothesis generation, experimental planning, execution, and interpretation. To address this, we develop and deploy a human-AI collaborative (HAIC) workflow that integrates large language models for hypothesis generation and analysis, with collaborative policy updates driving autonomous pulsed laser deposition (PLD) experiments for remote epitaxy of BaTiO₃/graphene. HAIC accelerated the hypothesis formation and experimental design and efficiently mapped the growth space to graphene-damage. *In situ* Raman spectroscopy reveals that chemistry drives degradation while the highest energy plume components seed defects, identifying a low-O₂ pressure low-temperature synthesis window that preserves graphene but is incompatible with optimal BaTiO₃ growth. Thus, we show a two-step Ar/O₂ deposition is required to achieve ferroelectric BaTiO₃ while maintaining a monolayer graphene interlayer. HAIC stages human insight with AI reasoning between autonomous batches to drive rapid scientific progress, providing an evolution to many existing human-in-the-loop autonomous workflows.

KEYWORDS: Autonomous synthesis, pulsed laser deposition, remote epitaxy, machine learning, large language models, barium titanate, *in situ* diagnostics, graphene.

INTRODUCTION

Autonomous and robotic laboratories are transforming materials synthesis by combining high-throughput experimentation and computation with machine learning to optimize processes^{1,2}. The prevailing paradigm imbues automated synthesis and characterization laboratories with decision-making driven by artificial intelligence (AI) to realize desired molecular and material properties while minimizing costly human intervention³. However, human-in-the-loop (HITL) has the potential to further advance AI/ML applications in industry⁴ and in materials characterization, such as X-ray phase mapping⁵ and atomic force microscopy (AFM)⁶, by bounding or initializing optimization procedures with human intuition within an automated experimental loop⁷. This improvement can be rationalized as arising from the incorporation of expert prior knowledge rather than the typically uninformative priors assumed by standard optimization algorithms. However, existing HITL workflows still suffer from significant drawbacks, with most being limited to an interventionist approach in which humans either seed initial experiments, modify parameter spaces, or inject knowledge at predefined points, limiting their utility. To leverage the rapidly developing capabilities of modern AI agents, more tightly coupled, collaborative workflows are required across all stages of the experimental process, from hypothesis generation and experimental planning to results interpretation that go beyond existing HITL workflows.

Here, we evolve HITL into human-AI collaborative (HAIC) workflows that couple human expertise, large language models (LLMs), and autonomous systems through mixed-initiative, between-batch loops. This approach is amplified by using LLMs alongside autonomous systems as “co-scientists”^{8,9} to help generate hypotheses, plan experiments¹⁰, and analyze data, especially when retrieval-augmented generation¹¹ (RAG) grounds the model in relevant scientific corpora¹². This flexibility is particularly suited to thin-film synthesis, where large parameter spaces with sparse prior data make defining robust success metrics challenging, especially when exploring new applications or materials systems.

Notably, thin-film synthesis poses a different set of challenges than materials discovery and requires a tightly coupled collaborative workflow. Success metrics may require complex measurements with bespoke analysis, defined iteratively rather than *a priori*, and are subject to significant data complexity (noise, unknowns, intangibles). Further, general mechanistic and experimental databases for thin-film synthesis are lacking, and literature-based recipes are often

too unreliable to predict performance metrics^{13,14}, making the incorporation of prior knowledge difficult. As data accumulates, the workflow must evolve to accommodate process improvement¹⁵ in all but the simplest scenarios to be effective. Addressing these challenges is essential to broaden the success and applicability of autonomous platforms, especially for thin-film synthesis.

Our work applies HAIC to autonomous synthesis, addressing key challenges in the emerging field of remote epitaxy (RE) of complex oxides by pulsed laser deposition (PLD). In RE, a two-dimensional interlayer, such as graphene, is placed on a single-crystal substrate, enabling the epitaxial growth of single-crystalline films that can be exfoliated as thin membranes and integrated on arbitrary substrates.¹⁶ However, PLD of complex oxides such as BaTiO₃ (BTO) requires growth conditions that destroy monolayer graphene interlayers, so successful PLD RE has relied on bilayer graphene to retain film transferability¹⁷⁻¹⁹. This poses a serious challenge for RE in PLD (and molecular beam epitaxy) because the transmitted electrostatic potential of the substrate through graphene is small ($\sim 10\text{-}20$ meV) and short-ranged (~ 2 Å)²⁰. Consequently, >1 graphene layers weaken or eliminate remote film alignment, yielding poorly oriented or polycrystalline films²¹, depending on the substrate’s ionicity/polarity^{22,23}. Comprehensive synthesis studies are essential to understand the limitations of oxide RE with PLD and aid the development of alternative strategies to enable remote epitaxy for arbitrary materials.

We deploy a HAIC strategy by combining state-of-the-art LLMs with an autonomous PLD system equipped with *in situ* diagnostics to understand how complex-oxide growth conditions drive graphene damage during RE, using BTO as a test case. LLM-assisted hypothesis generation, experimental design, and iterative process refinements enabled the autonomous campaign to efficiently map the parameter space and identify the BTO growth regime that minimizes graphene damage. Targeted *in situ* Raman experiments further elucidate the interplay of chemical interactions and ballistic damage in graphene defect generation during BTO deposition, providing a mechanistic basis for O₂-mediated RE with PLD. We also show that a two-step growth sequence minimizes graphene damage while yielding ferroelectric BTO. Together, these results show that a HAIC approach can rapidly close knowledge gaps in new fields and demonstrate its potential for application in any autonomous process that benefits from flexible, iterative policy updates led collaboratively by humans and AI.

RESULTS

Human-AI Collaborative Autonomous Synthesis Workflow

The HAIC autonomous synthesis workflow consists of 3 parts: AI-assisted generation of a testable hypothesis and a proposed experiment; fully autonomous PLD synthesis guided by Bayesian optimization (BO); and human-AI conferences for iterative data analysis and process improvement. First, we employed an LLM with a RAG pipeline to assist in literature summarization for hypothesis generation by prompting the LLM to identify research gaps in RE with PLD and to propose an experiment based on our experimental capabilities. **Figure 1a** shows a schematic of this AI-assisted hypothesis generation procedure. We compiled a curated knowledge base (KB) spanning scientific domains related to: RE in general, RE with PLD, Raman spectroscopy of graphene for defect analysis, PLD in general, PLD of BTO, autonomous experimentation, and Bayesian optimization. Curation of the KB involved (i) expert selection of relevant, trusted research articles and (ii) exclusion of tangential or low-relevance sources. During RAG, an embedding-based similarity search is used to retrieve KB passages from a diversity of sources that have high similarity to the query. The retrieved context is appended to the prompt to condition the LLM to prioritize information from the curated KB before defaulting to built-in knowledge or web search tools.

After hypothesis generation, we iteratively synthesized batches of samples via autonomous PLD, whose growth conditions were sequentially selected by BO, and reviewed the results via offline conferences with the LLM by prompting it with text, plot images, and raw data (**Figure 1b**). Here, “offline” specifies that the data transfer and prompts to the LLM were done by a human and not directly automated by the PLD software. Directly calling LLM-based analysis via the PLD software is simple to implement (an “agentic AI” platform), but the risk of costly, inevitable faults caused by the LLM in high-stakes experiments is unacceptable. In this context, “costly” refers to both time and financial cost (consumable materials). Example failure modes could be that the LLM repeatedly conducts experiments with parameters outside what a human expert deems feasible or a multimodal LLM misinterprets plot images used for experiment planning. Both example failure modes may lead to a reduction of experimental efficiency to or below that of random sampling. In this scenario, it is best to keep LLMs as “offline advisors” until their capabilities improve. Agentic platforms for lower-risk experiments like AFM could be immediately empowering. However, the

true benefit of this step is in the human-AI interaction via unstructured “chats”, collaborative data analysis, and AI-assisted human decision-making.

A schematic of the autonomous PLD system is shown in **Figure 1c** with details found elsewhere²⁴. This system combines automated PLD synthesis, multimodal *in situ* diagnostics, and substrate exchange with online machine learning for on-the-fly decision making post-growth or in real-time²⁵. Critically, the system is equipped with *in situ* Raman spectroscopy that is used to evaluate how the monolayer graphene interlayer accumulates damage during processing and/or BTO deposition (**Figure 1e**). The film growth rate varies by orders of magnitude depending on the conditions selected by BO. We use *in situ* laser reflectivity to control the thickness of each film to be nominally identical for fair comparisons across the dataset (**Figure 1d**). Lastly, an ion probe next to the substrate provides a measure of the kinetic energy of the plume, which is known to be a major factor in doping and damage of 2D materials in PLD²⁶⁻²⁸ (**Figure 1f**). Together, these diagnostics coupled with autonomy provide a unique opportunity to explore the relationship between oxide RE conditions and interfacial graphene damage.

The final AI-assisted hypothesis we selected is summarized here (paraphrased, **Note S1**). There exists a well-defined window of PLD growth parameters, specifically O₂ background pressure (pO₂), laser fluence (F), and substrate temperature (T_s), in which (a) the kinetic energy of the plume species falls below the displacement threshold of graphene (<~22 eV/C-atom²⁹) and (b) BaTiO₃ still nucleates in registry to the substrate through the graphene interlayer. In that window, the Raman defect metric I_D/I_G, the intensity ratio of graphene’s D and G bands measured by Raman spectroscopy, will remain small, and *ex situ* structural probes (i.e., XRD) will confirm remote epitaxy. Outside this window, either graphene damage increases or film registry is lost. The LLM suggests that fast neutral species³⁰ in the PLD plume will induce graphene defects (low pO₂, high F), high T_s (> 800 °C) will oxidize the graphene¹⁸, and too-low T_s will fail to crystallize BTO. To test this hypothesis, the LLM-suggested autonomous experiment was to deposit ~10 nm of BTO onto monolayer graphene/SrTiO₃ substrates with various pO₂ (50-250 mTorr), F (1.2-2.2 J cm⁻²), and T_s (650-800 °C) and conduct BO to minimize I_D/I_G.

We modified the AI-suggested experiment to explore lower T_s = 300-800 °C and used SiO₂/Si substrates to achieve high optical contrast for *in situ* laser reflectivity and to mitigate the difficulty in reliable quantification of I_D/I_G on SrTiO₃ (STO). The Raman R-band of STO dominates in the

same region as the graphene D/G bands¹⁸. SiO₂/Si does not provide the driving force for epitaxy, but we still found that BTO can grow oriented in some situations (**Figure S1**). The Gr/SiO₂/Si substrates were used exclusively to quantify graphene stability under PLD conditions via Raman spectroscopy. We supplemented the autonomous experiments with additional experiments on STO to test for substrate registry under replicated conditions. Finally, I_D/I_G is not an ideal optimization metric because: it cannot distinguish between defective graphene and amorphous carbon³¹; nor does it account for graphene loss via etching/oxidation; and does not account for variability in the initial graphene quality. Instead, we define a quality score based on the change in I_D/I_G, $\Delta = (I_D/I_G)_{final} - (I_D/I_G)_{initial}$ and define a retention ratio $r_G = I_{G,final}/I_{G,initial}$ which approximates how much graphene remains after deposition. The graphene quality is defined as $score = r_G/(1 + \Delta)$. We use BO to maximize this score, which is bounded from 0 to 1, where score = 1 indicates that the graphene was unchanged by the BTO deposition and score = 0 indicates that the graphene was destroyed.

Autonomous synthesis of BaTiO₃ with a monolayer graphene interlayer

Figure 2 shows the results of the human-AI-collaborative autonomous synthesis campaign of BTO on monolayer graphene/SiO₂/Si substrates. We grew a total of 37 films across 6 batches (phases) of 3-10 samples with no repeated growth conditions. Offline human-AI conferences were conducted after each phase. The first 3 sample conditions were chosen at random, and then we began BO using a Gaussian process (GP) surrogate model and acquisition function to propose the next (single) growth condition to maximize the graphene quality score. The final GP surrogate predictions, projected into each 2D parameter plane (mean of score over other planes), are shown in **Figure 2a-c** (**Figure S2** shows kernel-free surrogate model fits). The results clearly show that retaining a high-quality monolayer graphene interlayer in an O₂ environment requires low *p*O₂ and low T_s and is independent of F over the explored range. After phase I, the offline human-AI conference resulted in sequential refinement of the graphene Raman spectrum fitting procedure and provided monitoring of the optimization progress, identifying an early outlier result that strongly skewed the GP (**Note S2**). In parallel, human intuition based on expert-defined feasibility constraints on T_s and *p*O₂ was used to adjust the parameter bounds to align the BO exploration toward regions of interest, which are shown per phase in **Figure 2d**.

After the experiment, the final GP model was considered the “ground truth” and BO performance was quantified by comparing to 500 random sampling trials. In **Figure 2e,f**, the random curves are the mean of 500 trials, and the shaded area is the 95% confidence interval. We analyze regret at evaluation t : $r_t = f_p^* - f_p(\mathbf{x}_t)$ where f_p^* is the GP optimum in phase p within the active bounds and $f_p(x_t)$ are the GP predictions at that same step/phase/space. We report simple regret $s_t = \min_{i \leq t} (r_i)$ and cumulative regret $R_t = \sum_{i=1}^t r_i$. Small steps in simple regret occur at the boundaries between phases, a result from updated training data from refined curve fitting as well as GP surrogate improvement as data volume increases. **Figure 2e** shows the simple regret drops sharply after phase 1 and is near 0 after about 15 samples, beating the mean of the random trial baseline. **Figure 2f** shows the cumulative regret flattens at the same time, whereas the random case continues to increase. On average, BO reaches the optimum faster and accumulates fewer samples with low scores. Together, the surrogate maps and regret analysis demonstrate that the HAIC BO strategy efficiently discovered the low- pO_2 , low- T_s growth window while reducing frivolous experiments relative to random sampling.

We found the primary benefit of the human-AI conferences was the rapid iterative refinement of curve fitting methods used to calculate the Raman score (**Note S3, Table S1, Figure S3, Figure S4**). A major challenge in autonomous experiments is determining a “scalarizer” to convert high-dimensional data into a scalar value for optimization⁷. Here, the Raman score required a multi-peak curve fitting scalarizer. Generally, the data needed to develop a fitting routine robust against “unknown knowns” and “unknown unknowns” present in real spectra is not available prior to conducting experiments, and attempting to account for all conceivable data complexities a priori can be inefficient. Unexpected features or subtle physical effects may arise that are not captured in prior models⁷. Though exploratory measurements can help build a diverse dataset early on³², ongoing quality checks and further refinement during optimization remain crucial to ensure robust model performance. A practical approach is to begin collecting data and iteratively refine the fitting routine on-the-fly using a HAIC workflow. This development may be needlessly time consuming if attempting to account for all conceivable data complexities. A better approach is to begin collecting data and refine on-the-fly with a HAIC workflow. Without the offline human-AI conferences, the experiment (as initialized) would have failed if run in a fully autonomous modality due to early outliers caused by a non-robust scalarizer.

Contributions of plume kinetic energy and reactive chemistry to graphene damage

We probe the origin of the graphene damage with *in situ* Raman spectroscopy by correlating defect metrics with plume kinetic energy, background gas, and temperatures, and we support this interpretation with molecular dynamics (MD) simulations. **Figure 3a** compares ion probe traces in 60 mTorr O₂/Ar and vacuum. The probe traces exhibit a clear plume splitting into “fast” and “slow” components³³. In vacuum, the plume has a “fast” component (~108.5 eV/Ba-atom, most probable kinetic energy (MPKE) taken from the time-of-flight of the peak) arising from ballistic species with no gas-phase scattering. In Ar and O₂, a fraction of the “fast” component is scattered, producing an additional “slow” component (~6.6 eV/Ba-atom MPKE in both Ar and O₂). The “slow” component MPKE is tunable with pO₂ and F but is always below the C displacement threshold (**Figure S5**). **Figure 3b** shows the change in I_D/I_G during BTO deposition in 60 mTorr O₂/Ar at temperatures from 20-500 °C. The I_D/I_G rises steeply in O₂, especially at elevated temperatures, while Ar produces a markedly shallower slope. The plume kinetic energy distribution is similar in both gases at this pressure, indicating that an Ar background suppresses the degradation that occurs rapidly in O₂. Bombardment of the graphene/SiO₂ by the “fast” component was simulated by MD, which shows that some vacancies and disorder are caused by the plume, but it does not destroy the graphene (**Figure 3c**). We also tested the maximum energy (plume leading edge, 318 eV/Ba-atom) which caused more disorder (**Figure S6**) but without complete destruction.

The ballistic damage alone does not account for the complete etching of graphene that we observe at high temperatures. **Figure 3d** shows the evolution of the Raman spectrum vs pulses during BTO deposition at 500 °C in O₂ and Ar. In O₂, the graphene D mode intensity rapidly grows, decreases, and vanishes concomitantly with the G mode, indicating a full amorphization trajectory and etching of graphene. In Ar, defects form but the graphene is not amorphized/etched. At 300 °C and 20 °C, we do not observe etching, suggesting a thermally activated oxidation process (**Figure S7**). We also ran no-deposition controls (**Figure S8**). During annealing in Ar and O₂ (**Figure S8a, b**), no D band appears up to 700 °C, indicating thermal cycling alone does not create significant point defects.

MD simulations of the oxidation of pristine and 2% C-vacancy graphene show that O species adsorb to graphene and attack C-vacancy sites, forming CO₂ that desorbs over time (**Figure 3e**).

We conducted temperature-dependent simulations from 20-800 °C, measured the number of C atoms that leave the system, and found agreement with experiments (**Figure 3f**). First, MD confirms that pristine graphene does not oxidize up to 800 °C. Second, we observe a thermally activated oxidation process in which the number of C atoms leaving the monolayer increases exponentially with temperature, with complete etching at 800 °C.

These comparisons make the kinetic energy-chemistry-damage relationship explicit and underscore that the damage induced by plume kinetic energy is independent of the damage via chemical reactivity, though it must assist oxidation in an O₂ environment. Energetic O species in the plume are not a primary cause of graphene oxidation; only the highest MPKE plume components cause ballistic damage to the graphene. The fast component of the plume must still damage the graphene at higher pressures, but the rate is significantly decreased due to order-of-magnitude attenuation in the number of fast particles. However, these plume-induced vacancies are highly reactive to O₂, resulting in a defect cascade that accelerates with temperature.

Two-step deposition for epitaxial ferroelectric BTO with monolayer graphene interlayer

Figure 2 established that preserving monolayer graphene during oxide PLD requires low-pO₂ and low-T_s, while **Figure 3** traced the protection afforded by Ar at least up to 700 °C. Building on this, we first assessed whether one-step O₂ growth at reduced T_s could yield crystalline BTO on (001) STO. XRD θ -2 θ scans in **Figure 4a** show that the BTO 002 reflection is weak or absent below 500 °C and strengthens as T_s increases, indicating that the minimum temperature required for BTO crystallization on STO is between 400-500°C. Quantitative fitting of the BTO 002 peak (**Figure S9**) reveals a monotonic decrease in FWHM with increasing T_s, confirming improved out-of-plane crystalline quality at higher growth temperatures. This constraint conflicts with preservation of graphene in O₂, motivating a two-step approach in which a seed-layer is first grown in Ar and followed by continued growth in O₂, suggested by Lee et al.³⁴. The results of this two-step growth at 700 °C are shown in **Figure 4b** (**Figure S10a** shows X-ray reflectivity). X-ray reflectivity measurements (**Figure S10a**), fit using Parratt's formalism implemented in GenX 3^{7,35,36} using a procedure similar to Carpenter et al.³⁶, confirm a continuous BaTiO₃ film with a thickness of 50.7 nm. The BTO 002 peak confirms that the two-step route preserves BTO crystallinity, even though it was partially grown in an O-deficient environment. Raman measurements verify that graphene is not fully etched by this process: the Gr/SiO₂/Si reference sample exhibits a strong G mode with

low D to start, and after two-step BTO growth at 700 °C the G band remains visible with a moderate D band (**Figure 4c-d**), consistent with partial disorder. This approach also enabled exfoliation of the BTO film using monolayer CVD-grown, wet-transferred graphene, as confirmed by the XRD and optical image in **Figure 4b** (literature comparison in **Table S2**).

Finally, piezoresponse force microscopy (PFM) utilizing interferometric detection to minimize cantilever-driven electrostatics show that BTO films grown by the two-step deposition method maintain a ferroelectric polarization. Application of -10 V through the scanning probe tip reverses the polarization, suggesting the sample polarization is initially down-oriented (application of +10 V shows no change from the non-switched regions) (**Figure 4d, S10b**). Ferroelectricity is further established through switching spectroscopy PFM (SS-PFM) measurements, which reveal hysteresis behavior with 180° phase reversal and a coercive voltage of $\sim \pm 1.5$ V (**Figure 4e**); this behavior disappears when heated above the Curie temperature (**Figure 4f**). Together with the *in situ* Raman study (**Figure 3**), these results show that Ar in the first step limits both ballistic damage and oxidation of graphene, and the subsequent O₂ step maintains O-stoichiometry to achieve ferroelectric BTO.

DISCUSSION

We demonstrate a human-AI collaborative (HAIC) autonomous synthesis workflow that combines retrieval-augmented LLM hypothesis generation and analysis with an autonomous PLD platform to study RE of complex oxides. In the BTO/graphene system, the HAIC campaign efficiently links growth conditions to graphene damage and, together with targeted *in situ* Raman and plasma plume measurements, shows that gas chemistry dominates overall degradation while ballistic impacts seed reactive defects; this isolates a low-pO₂, low-T_s regime that preserves graphene yet conflicts with optimal BTO growth. Guided by this insight, a two-step Ar/O₂ sequence is required and can yield ferroelectric, crystalline BTO while maintaining the graphene interlayer. Beyond the specific application, the value lies in the pattern of work: humans and AI collaboratively set objectives, refine processes and analyses between autonomous batches, and redeploy updated policies to achieve rapid and efficient scientific progress. The same HAIC approach transfers to other autonomous platforms and will strengthen with the fast-paced improvement of language models, enabling more reliable and data-efficient autonomous experimentation.

METHODS

Retrieval Augmented Generation

Text from 345 articles and supplemental information files were extracted, filtered, split into 300-token chunks with a 30-token overlap, and embedded as 3072-dimensional feature vectors using OpenAI’s text-embedding-3-large model. The user query was embedded with the same model and maximal marginal relevance (MMR) search is used to retrieve the top 50 most similar text chunks, balancing high similarity to the query with diversity of sources, with the MMR trade-off parameter set to $\lambda = 0.3$. These chunks were appended to the initial query to form the full LLM prompt. The LLM was accessed through the OpenAI Responses API using the GPT-5 snapshot gpt-5-2025-08-07 with high reasoning effort enabled (thinking mode). Generation was performed with a temperature of 0.3, while top_p and max_output_tokens were not manually tuned and were left at OpenAI API default values. We developed an open-source, user-friendly graphical interface package that constructs a knowledge base from a collection of PDFs and performs RAG with ChatGPT (requires an OpenAI API key). The package can be downloaded from https://github.com/sumner-harris/RAGAgent_AutonomousMaterialsSynthesis.git

Bayesian Optimization

Bayesian optimization is carried out using a custom python package (ALchemy) built using BoTorch³⁷ with a single task Gaussian process regression model implemented via GPyTorch³⁸. Input features $\mathbf{x}$ are normalized [0,1] per dimension and the target was standardized to zero mean and unit variance for training. The GP prior used a learned constant mean function and a radial bias function (RBF) kernel with automatic relevance determination (ARD) wrapped in a scale kernel:

$$k(\mathbf{x}, \mathbf{x}') = \sigma_f^2 \exp\left(-\frac{1}{2} \sum_{i=1}^d \frac{(x_i - x'_i)^2}{\ell_i^2}\right)$$

where σ_f is the target variance and ℓ_i is the length scale of each dimension. GP hyperparameters (mean constant, target scale, length scales, and noise) were learned by maximizing the marginal likelihood on the transformed data. The autonomous synthesis campaign was posed as a maximization problem and used the Monte Carlo formulation of the log expected improvement

acquisition function³⁹ (qLogEI), implemented via BOforch. ALchemy is freely available at <https://github.com/sumner-harris/alchemy.git>

CVD Growth of Graphene on Cu

Monolayer graphene was synthesized by atmospheric-pressure chemical vapor deposition (AP-CVD) on copper foil following the ORNL recipe. In brief, 25-125 μm Cu foils were solvent-cleaned (acetone, isopropanol) and electropolished in 85 % H_3PO_4 at 1.9 V for 30-60 min, then rinsed with DI water and IPA and dried. Foils were loaded into a horizontal quartz-tube furnace and pre-annealed at 1000 °C for 1 h in a forming-gas carrier (2.5 % H_2 in Ar; total flow $\sim 5 \text{ L min}^{-1}$). Growth proceeded at 1000 °C by stepwise CH_4 dosing in the H_2/Ar carrier to suppress multilayers: CH_4 (1000 ppm in Ar) was metered to give 30, 50, 70, and 100 ppm at the reactor inlet, 45 min per step (total $\sim 3 \text{ h}$) while maintaining the same total flow. At the end of growth, the furnace was opened to accelerate cooling under H_2/Ar . This is adapted from Vlassioug et al.⁴⁰, which details the role of Cu pretreatment, staged methane dosing, and lamination-based transfer for large-area monolayer graphene.

Wet Transfer of Graphene

The as-grown graphene on the copper foil was spin-coated with PMMA at a speed of 2000 revolutions per minute (rpm) and left to cure at room temperature for 24 hours. An ammonium persulphate solution was employed to etch the copper foil. The remaining graphene, along with the PMMA layer, was transferred to HCl and then to DI water to dissolve any salt residue. The cleaned graphene was subsequently collected and dried on the desired substrate. The PMMA layer was removed by immersing it in acetone and then rinsing it with fresh acetone and isopropyl alcohol to eliminate any PMMA residue. After transfer, a Raman spectrum was collected of the graphene to confirm that it is monolayer, indicated by a 2D/G band ratio > 2 (**Figure S11**)

Pulsed Laser Deposition

Film growth: BTO films were deposited by PLD using a KrF excimer laser (248 nm, 25 ns, 5 Hz; Coherent LPX 305F) to ablate a stoichiometric BTO target. The target-substrate distance was 5.0 cm, and the substrate temperature was varied from 300-800 °C. Laser fluence at the target was set with a motorized attenuator and bidirectional slits on a projection beamline, defining a spot on the target (area 0.022 cm^2) into which all the laser energy that was directed into the deposition chamber (44 mJ in the case of 2 J/cm^2) was deposited - i.e., a top-hat beam profile scenario. Background

gas during deposition were either Ar (99.999%, 5 sccm) or O₂ (99.999%, 5 sccm). Gas flow values specified in the text were established with mass-flow controllers and the total pressure was maintained with a throttle valve. The base pressure prior to each set of ten depositions was $< 5 \times 10^{-6}$ Torr. Substrates were bonded to Inconel carrier plates that were heated from the backside with a 976 nm, 140 W diode laser, and temperature was controlled in a closed loop fashion with a backside pyrometer with an accuracy of ± 1 °C. Front-side temperature (or approximately the substrate temperature) was independently confirmed with either a spot-welded fine gauge thermocouple and Raman shift vs temperature measurements on Si.

Plume diagnostics. Ion-probe waveforms were measured with a biased wire probe (-40 V bias; 4 mm length, 0.4 mm diameter) placed adjacent to the substrate with a 4.5 cm target-probe distance. The probe current was recorded on a 1 GHz oscilloscope (Tektronix MSO64) across a 50 Ω feed-through BNC terminator. The oscilloscope was triggered by a fast photodiode monitoring the KrF laser pulses.

In situ Raman Spectroscopy

A 532 nm continuous wave laser (Cobolt Samba, 1 W max, Huber Photonics) was used to excite the samples at 55° angle of incidence. The laser spot on the samples was elliptical (0.7 mm $\times$ 0.6 mm) with the major axis aligned with the spectrometer slit. Raman scattered light was collected at normal incidence and imaged onto the spectrometer slit with a 75 mm diameter, $f = 350$ mm spherical lens mounted inside the chamber. A long-pass edge filter (Semrock, RazorEdge) was used to filter the laser line. The spectrometer (Princeton Instruments, Isoplane SCT 320) was coupled with a CCD detector (Princeton Instruments, PIXIS 400BRX) and used a 2400 grooves per mm holographic grating. The laser power and CCD exposure times for all samples and reference spectra were 300 mW and 15 s exposure, 4 averages.

In Situ Reflectivity Optical Contrast Modeling

Reflectivity was monitored *in situ* using a stabilized, randomly polarized HeNe laser (632.8 nm, 1.2 mW; HRS015B, Thorlabs, Inc.) incident at 32.5°. A liquid crystal polymer depolarizer (DPP25-B, Thorlabs, Inc.) was used to ensure random polarization. The reflected signal was filtered through a laser line filter (FL632.8-1, Thorlabs, Inc.) and detected using a silicon photodiode (SM1PD1B, Thorlabs, Inc.) connected to a source measure unit (2450, Keithley Instruments). Data were recorded continuously, with a 10 second pre-deposition baseline used to

determine the average initial signal, I_0 . Real-time optical contrast was calculated as $C(t) = (I(t) - I_0) / I_0$ where $I(t)$ is the photodiode current at time t . Deposition was terminated automatically when $C(t)$ reached the target contrast value corresponding to 5 nm of BTO.

The optical contrast of the Vacuum/BTO/graphene/SiO₂/Si multilayer stack was modeled using the transfer matrix method (TMM), which calculates the Fresnel reflection coefficients recursively across stratified media. The total reflectance was computed for both s- and p-polarized light and averaged to represent randomly polarized illumination. Refractive indices used at a wavelength of 632.992 nm were: Si ($3.872 + 0.016i$), SiO₂ (1.4689 and 270 nm thickness), monolayer graphene ($2.6 + 1.3i$), and BTO ($2.38 + 0.01i$). The BTO film thickness for the BO optimized films were kept for 5.25 nm, corresponding to ~13-unit cells based on a c-axis lattice parameter of 0.404 nm (**Figure S12**).

The calculated reflectance contrast for a 5.25 nm-thick BTO film on this substrate configuration was -0.203, which was used as the target threshold for terminating growth in real-time during deposition. Temperature-dependent variations in refractive index were neglected. Simulations showed that angular uncertainty of $\pm 2.5^\circ$ from the nominal incident angle of 32.5° resulted in negligible variation in the calculated contrast, remaining below the experimental noise floor.

Ex situ Characterization of Thin Films

XRD and XRR were done with a PANalytical X'pert PRO MRD diffractometer implementing a hybrid monochromator (Cu K α_1) with a $1/8^\circ$ and $1/32^\circ$ divergence slit, respectively. A 0.27° parallel plate collimator with 0.04 radian Soller slits were used on the detector (Xe proportional counter) side in both cases and an additional 100 μm receiving slit for XRR.

PFM was performed in an Oxford Instruments Asylum Research Vero with an Environmental Scanner using a BudgetSensors ElectriMulti75-G Pt-Si tip. Measurement was performed off-resonance with a drive amplitude of 500 mV. To gather temperature-dependent SS-PFM data, the sample was heated to 250°C , which was verified with a thermocouple. Data was collected off-bias at 0.1 Hz and with a 2-V drive oscillation. 3 consecutive loops were taken at five random locations; the presented data is the average of 15 separate loops. The sample was then cooled below 100°C and measurements were repeated. SS-PFM data was plotted using pre-built functions in the *Hystorian* package⁴¹.

Molecular Dynamics Simulations

The MD simulations were performed using the LAMMPS⁴² MD simulation package. For the impact simulations, the AIREBO⁴³ potential was used to describe graphene, and the Tersoff⁴⁴ potential was employed for the amorphous SiO₂ substrate, while the interactions between the graphene monolayer and the substrate were described using Lennard-Jones⁴⁵ (LJ) parameters, similar to Zhao and Xue⁴⁶. Short-range repulsive Ziegler-Biersack-Littmark⁴⁷ (ZBL) potentials were used in all pair interactions, including the interactions with the projectile, Ba. The size of the systems used for the impact simulations was about 10.1 nm × 10.2 nm. The substrate size was 5 nm, and the graphene monolayer contained about 4000 atoms. The systems were relaxed and then equilibrated at 600 °C (873.15 K). Projectile energies of 139 eV/Ba-atom and 318 eV/Ba-atom (approximately the maximum observed) were used to study the ballistic defect formation. A total of 200 Ba ions and a total of 133 Ba ions were used for each energy, respectively. The impact of the ions with the system was simulated in the microcanonical ensemble (NVE), with a 5 ps interval between successive ions, which was sufficient for system thermalization. A variable timestep was used to account for the impact dynamics, with a maximum value of 0.5 fs. Periodic boundary conditions were applied along the x and y dimensions of the MD box.

For the annealing simulations, a ReaxFF force field for graphene and oxygen interactions⁴⁸ was utilized in a triclinic simulation cell was used with periodic boundary conditions applied along the x and y directions and a free surface along z in vacuum, with cell dimensions of about 49.3 Å (x-axis) and 42.7347 Å (y-axis). The system consisted of a graphene bilayer, where the bottom monolayer was thermostatted to mimic the thermal response of a substrate. The top monolayer was left unrestrained and interacted directly with the incoming gas species. In the figures only the upper monolayer is shown for simplicity, since the lower monolayer is thermostatted and does not interact with the gas. The annealing simulations were performed at 0 °C (273 K), 300 °C (573 K), 600 °C (873 K), 700 °C (973 K), and 800 °C (1073 K), after prior equilibration of each system at the corresponding temperature. Annealing simulations were performed under the NVE ensemble using a variable timestep (maximum 0.25 fs) to capture fast dynamics that may occur. To simulate the gas, we inserted 1000 O atoms with intervals of 125 fs. The total simulation time at each temperature was about 1 ns.

Exfoliation of BaTiO₃

To exfoliate the BTO film, a 2.7 μm thick Ni stressor layer was deposited on the two-step-grown BTO/Gr/STO heterostructure using DC magnetron sputtering at 30 W, under a base pressure of 1×10^{-6} Torr. The resulting Ni/BTO stack was subsequently exfoliated using a thermal release tape (TRT). The inset of **Figure 4b** displays the exfoliated BTO/Ni layer adhered to the TRT.

DATA AVAILABILITY

The data that support the findings of this study are available upon reasonable request.

CODE AVAILABILITY

The code used for Bayesian optimization and surrogate models in this study are openly available through the ALchemy package at <https://github.com/sumner-harris/alchemy.git> and the user interface software for RAG using the OpenAI API for ChatGPT are available at https://github.com/sumner-harris/RAGAgent_AutonomousMaterialsSynthesis.git

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AUTHOR CONTRIBUTIONS

A.H.: Conceptualization (equal), Investigation (equal); Writing-Original Draft (equal); Writing-Review & Editing (equal). **D.T.Y.:** Investigation (supporting), Writing-Original Draft (supporting). **J.C.:** Investigation (supporting); Software (supporting). **R.B.:** Investigation (supporting). **I.V.:** Investigation (supporting). **J.L.:** Investigation (supporting). **S.G.:** Investigation

(supporting). **C.M.R.**: Investigation (supporting). **K.X.**: Writing-Original Draft (supporting). **Y.L.**: Investigation (supporting). **E.Z.**: Investigation (supporting). Writing-Original Draft (supporting). **R.K.V.**: Writing-Original Draft (supporting); **S.B.H.**: Conceptualization (equal); Investigation (equal); Methodology (lead); Software (lead); Writing-Original Draft (equal); Writing-Review & Editing (lead). All authors have read and approved the manuscript.

COMPETING INTERESTS

The authors declare no competing financial or non-financial interests.

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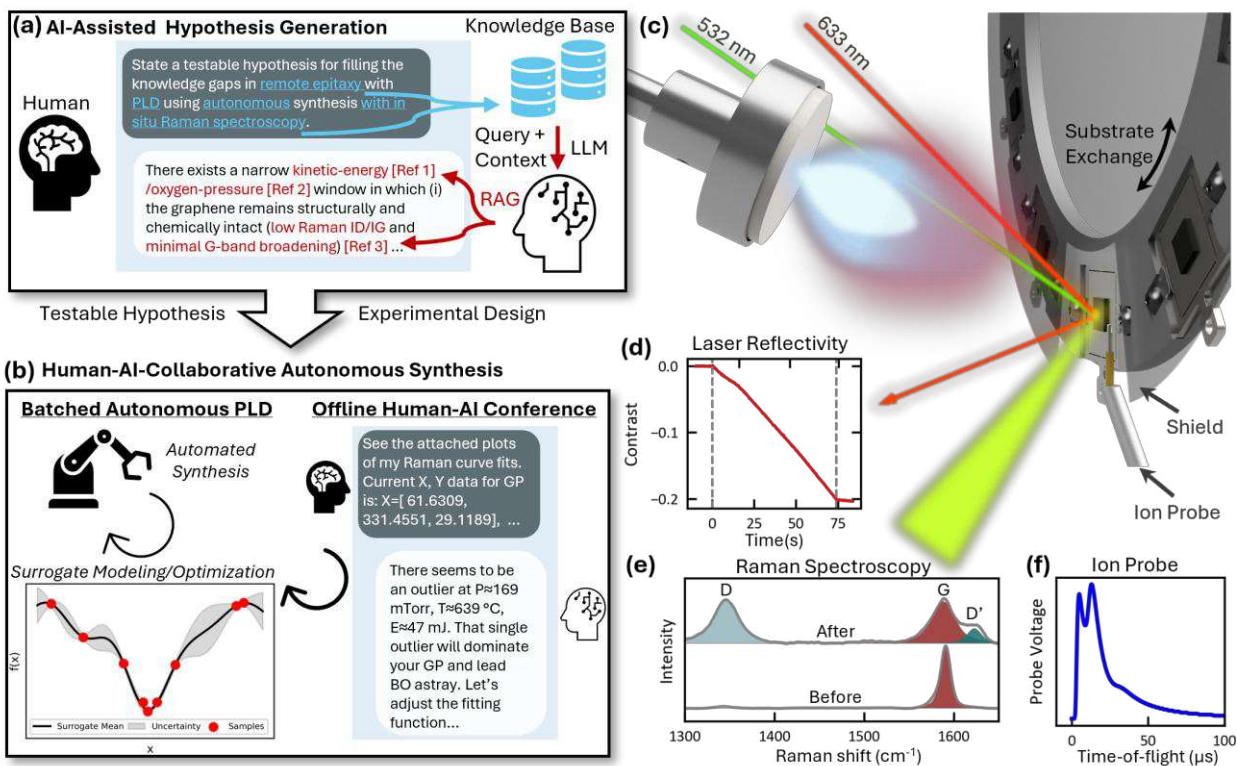


Figure 1. AI-Assisted hypothesis generation and human-AI collaborative (HAIC) autonomous synthesis. (a) A curated domain-specific knowledge base is queried via retrieval-augmented generation (RAG), and the human expert and LLM engage in an iterative refinement loop to converge on a final testable hypothesis and initial experimental design. (b) HAIC autonomous synthesis is conducted which combines fully autonomous synthesis with human-AI conferences to cooperatively analyze data and refine the active learning procedure. In online active learning, an autonomous batch of PLD synthesis with *in situ* characterization is conducted using Bayesian optimization to drive the sequence of experiments in the batch. The offline conferences between the human and LLM are conducted to review the collected data suggest and adjust the surrogate model/acquisition function/target as needed back into the next batch of autonomous PLD. (c) Schematic of the PLD chamber highlighting the multi-substrate exchange mechanism, enabling batch depositions up to ten substrates without breaking vacuum. This is integrated with *in situ* diagnostics, (d) including laser reflectivity, (e) Raman spectroscopy, and (f) ion-probe measurements, enabling high-throughput, closed-loop synthesis and characterization.

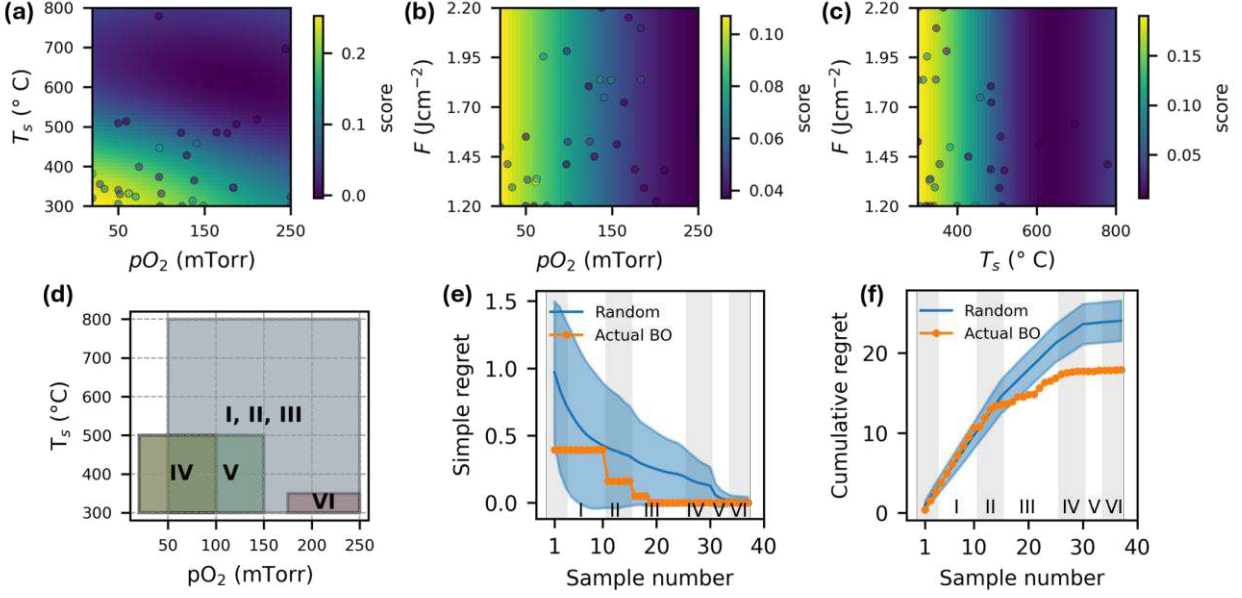


Figure 2. Human-AI collaborative (HAIC) autonomous synthesis campaign of BaTiO₃ on monolayer graphene/SiO₂/Si substrates. The final Gaussian process (GP) surrogate model predictions for the graphene quality *score* = $r_G/(1 + \Delta)$ (r_G is the retention ratio and Δ is change in I_D/I_G) in the parameter space are shown projected into the (a) substrate temperature T_s vs. oxygen pressure pO_2 plane, the (b) laser fluence F vs. pO_2 plane, and the (c) F vs. T_s plane. To retain high monolayer graphene quality, low- T_s , low- pO_2 growth is required, and is essentially independent of F . The HAIC synthesis campaign used offline human-AI conferences resulting in experimental phases with sequential improvements to Raman analysis and dynamic parameter bounds for batches of samples. The parameter bounds for optimization in each of the 6 experiment phases are shown in (d). The simple (e) and cumulative (f) regret of the actual Bayesian optimization (BO) results compared to 500 random trials (using the final GP surrogate model as ground truth) confirms the BO outperformed random sampling, with each phase represented by the gray/white shaded regions. The 95% confidence bound is plotted with the mean of the random trials.

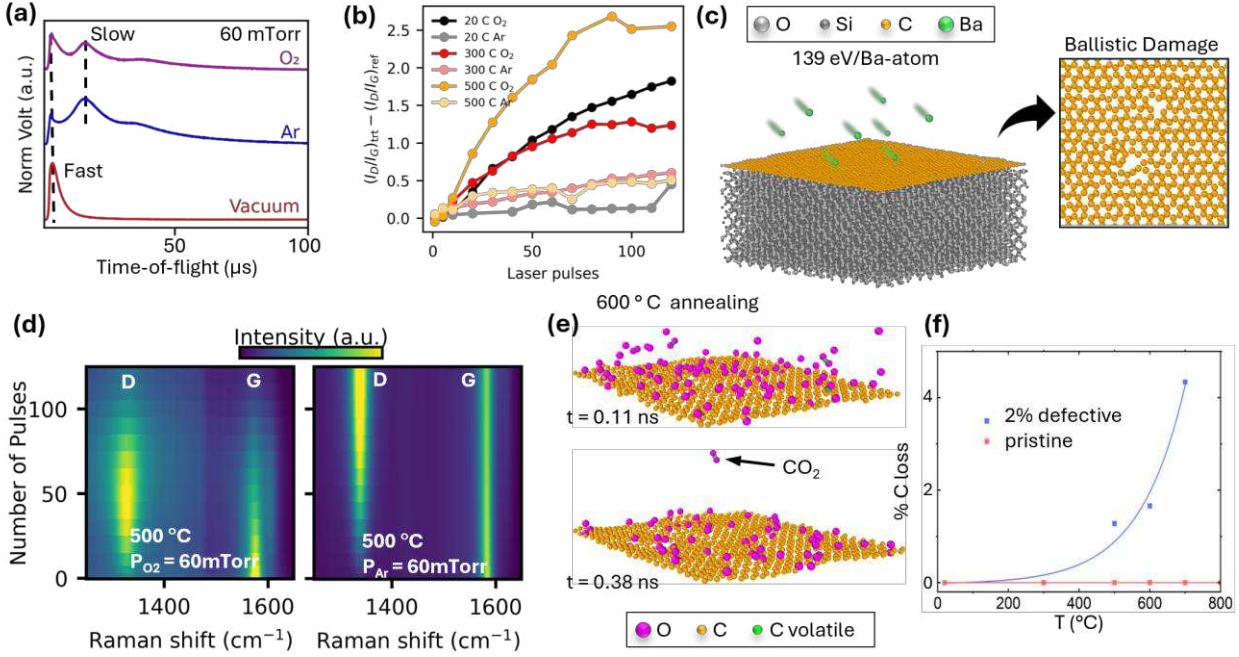


Figure 3. The interplay of chemical reactivity and plume-induced ballistic damage dictate graphene degradation. (a) Ion probe traces (4.5 cm from the target) in O₂, Ar, and vacuum. (b) Evolution of the Raman defect metric Δ (the change in I_D/I_G) versus laser pulses in O₂ and Ar at different substrate temperatures (60 mTorr). (c) Molecular dynamics (MD) simulations of Ba bombardment on graphene/SiO₂ shows C vacancy generation and disorder. (d) Raman heatmaps vs laser pulses at 500 °C for O₂ and Ar show that graphene is etched during BaTiO₃ deposition in O₂ but not in Ar. (e) MD simulations of graphene oxidation shows that 2% C-vacancy graphene is rapidly etched at high temperatures while pristine graphene is unreactive. (f) C loss vs temperature calculated from MD simulations show a thermally activated oxidation process.

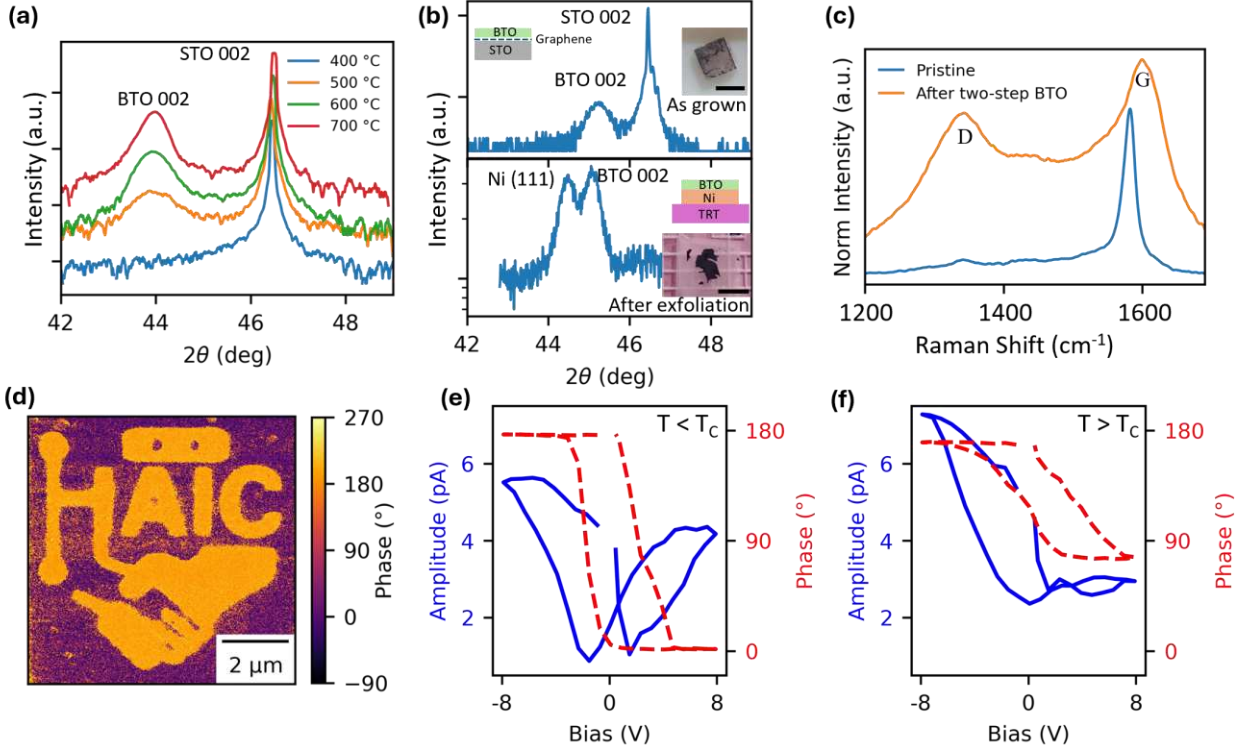


Figure 4: Two step growth enables crystalline BaTiO₃ while preserving graphene. X-ray diffraction θ -2 θ scans around SrTiO₃ 002 (a) one-step BaTiO₃ growth on SrTiO₃ with different substrate temperature, (b) 50.7 nm thick BTO film by two-step growth (first in Ar, then in O₂) at 700 °C followed by exfoliation of the BTO/Ni (stressor layer) exfoliation with the thermal release tape (TRT). Inset shows the cross section of the heterostructure and optical image (scale bar 5mm) (c) Raman of Gr/SiO₂/Si reference at 150 °C before deposition, and after two-step growth shows a retained G band and moderate D band increase, indicating graphene is not fully etched. (d) Patterning via piezoresponse force microscopy (PFM) shows clear polarization reversal. (e) Switching spectroscopy PFM (SS-PFM) amplitude and phase taken below the Curie temperature (T_C) show clear ferroelectric at ± 2 V. (f) Above the ferroelectric phase transition, polarization reversal was not apparent, verifying ferroelectric behavior below T_C .

Supplementary Files

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