

LOW-COST, SINGLE-STEP VAPOR DEPOSITION OF THIN FILM ORGANIC PEROVSKITES FOR SOLAR AND MEMRISTOR APPLICATIONS

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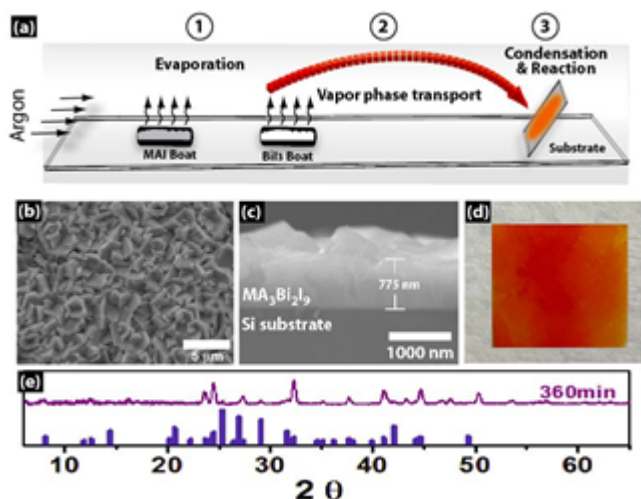
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Technology Description

Engineers in the Banerjee laboratory have developed a single-step, scalable vapor deposition process for fabricating high performance thin film perovskite materials at low temperature and atmospheric pressure. These lead-free, non-toxic films could be used as solar cell absorbers or in memristors for fast, non-volatile resistive random-access memory (ReRAM).

Currently, lead halide perovskite solar cells provide high performance. However, the materials are not stable and manufacturing is difficult to scale because they contain toxic lead materials. Alternative non-toxic organic halide (bismuth) perovskites are non-toxic but current solution-based fabrication techniques are woefully inadequate for scale-up and manufacturing. This invention solves these problems with a single-step gas-phase deposition that can be used to fabricate methylammonium bismuth iodide ($\text{MA}_3\text{Bi}_2\text{I}_9$) and other perovskite thin films with better control over morphology, purity and coverage. The resulting thick, n-type semiconductor films are superior to solution-processed, undoped films with an indirect optical bandgap of 1.80 eV.

Furthermore, these thin films could be used to create organic-inorganic hybrid materials in a flexible memristor device with high performance switching. The hybrid memristors have ON/OFF ratios up to 10^5 which is achieved through a different resistive switching mechanism than current ReRAM materials. End-user applications of these materials include internet of things (IoT) devices, low power ASCII hardware, and neuromorphic computing.



Perovskite deposition for memristor application: (a)

Schematic of APCVD process to deposit MA₃Bi₂I₉ films (b, c and d). Top-down and cross-section of SEM shows well developed dense, crystalline grains and an optical image and (e) X-ray diffraction of the film deposited confirming MA₃Bi₂I₉ phase.

Stage of Research

For solar application: The inventors fabricated and characterized MA₃Bi₂I₉ and found the n-type semiconductor films to be superior to solution-processed, undoped films. The 775nm thick films had an indirect optical bandgap of 1.80 eV; a room temperature excitonic peak at 511 nm; carrier concentration of $3.36 \times 10^{18} \text{ cm}^{-3}$; and a Hall mobility of $18 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. In addition, the inventors demonstrated flexible deposition on Willow glass.

For memory/memristor application: The inventors fabricated a memory device using MA₃Bi₂I₉ (MBI) thin films as an active layer. They demonstrated resistive switching behavior including low SET voltage (0.15V), high ON/OFF ratio (up to 10^5) over 1000 cycles, long-term retention property ($1.6 \times 10^4 \text{ s}$) and high frequency operability (as high as 10^4 Hz).

Applications

- **Photovoltaics** – solar cell absorber materials
- **Computer memory** – memristor material for fast, non-volatile resistive random-access memory (ReRAM), particularly in internet of things (IoT), low power ASCII hardware or neuromorphic computing applications

Key Advantages

- **Low-cost, single-step, scalable deposition process:**
 - low temperature (160°C)
 - atmospheric pressure (no vacuum)
 - possible to deposit films in high volume, cleanroom compatible manufacturing settings
 - process can be used for a broad range of perovskite compositions, including organic-inorganic hybrids
- **High-performance, flexible material:**
 - for photovoltaic application: indirect optical bandgap of 1.80 eV
 - for memory/memristor application: ON/OFF ratio up to 10^5 over 1000 cycles
 - dense, high quality organic/inorganic hybrid film combines flexibility and low-cost synthesis of organic with high mobility, crystallinity and thermal stability of inorganic constituents
- **Environmentally-friendly** - material comprised of non-toxic bismuth instead of lead

Publications

- Chen, X., Myung, Y., Thind, A., Gao, Z., Yin, B., Shen, M., ... & Banerjee, P. (2017). [Atmospheric pressure chemical vapor deposition of methylammonium bismuth iodide thin films](#). Journal of Materials Chemistry A, 5(47), 24728-24739.

Patents

- [Chemical vapor deposition of perovskite thin films](#) (Patent US11,094,881)