Mist-CVD Growth of Gallium Oxide for Developing Solar-Blind UV Photodetectors for International Safeguards Applications

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Abstract

Gallium oxide (Ga_2O_3) is a compelling candidate material for radiation detection, particularly for the ultraviolet (UV) portion of the electromagnetic spectrum. Its exceptionally wide bandgap (up to 4.9 eV) renders it insensitive to thermal excitation. Moreover, as a compound semiconductor, the bandgap of gallium oxide can be tuned to further tailor its response spectrum to a given application, such as allowing for the isolation of signals in the deep UV. Furthermore, because of its radiation hardness, gallium oxide's solar-blind functionality can be employed even in harsh environments. While solar-blind UV photodetectors have been studied extensively for uses in corona discharge detection, communications, and more, their uses in international safeguards have been underemphasized.

Solid-state detection of Cerenkov light is at the heart of the International Atomic Energy Agency (IAEA) inspector's modern toolkit. The Digital Cerenkov Viewing Device (DCVD) scans for bulk and partial defects in spent light-water reactor (LWR) fuel rods stored in cooling pools. Unfortunately, external filtration incurs large signal losses and still permits infrared leakage. Additionally, the DCVD lacks a tunable bandgap and has a poor radiation hardness that precludes it from submersion into a strong radiation field. To confront these shortcomings, we are developing a Cerenkov detector made from α-Ga_2O_3 and grown by mist chemical vapor deposition (mist-CVD). Mist-CVD has the advantage of low cost and relative simplicity and is well-suited to the lower temperature growth of the α-phase polymorph. This is done with the aim of eliminating noise like indoor fluorescent lighting while harnessing Ga_2O_3's solar-blind imaging capabilities.

Introduction

Cerenkov Detection and International Safeguards

Cerenkov light is the consequence of any charged particle exceeding the speed of light within a given medium. In such an event, the medium's refractive index can reduce this limit to lower than that experienced by light in a vacuum. This can be thought of as the optical analogue to the sonic effect of breaking the sound barrier. Cherenkov light emissions result when a charged particle polarizes the medium within which it travels, in turn releasing a shockwave of light that propagates outward from its path. In water, escaping Cerenkov light consists of the far end of the visible spectrum and a large portion of the ultraviolet (UV), producing the familiar blue glow associated with nuclear reactor operation.

The relevance of this phenomenon to nuclear materials management is well established, especially in the context of spent fuel assemblies placed in interim storage in cooling ponds. While underwater, irradiated light-water reactor (LWR) fuel rods undergo beta decay that results in Cherenkov signatures that can be interpreted by IAEA personnel during safeguards inspections. Therefore, several devices have been developed to exploit the phenomenon for the purpose of verifying the non diversion of LWR spent fuel. Beginning with the Cherenkov Viewing Device (CVD), advances in detector technology eventually led to the current state-of-the-art Digital Cerenkov Viewing Device (DCVD), which operates via a Si charge-coupled device (CCD). Both have the capacity to identify bulk defects —scenarios in which an entire fuel assembly is missing— but the DCVD could do the same for partial defects as well. Example scenarios include detecting whether an individual fuel rod has been removed or replaced with a dummy. The use of advanced CCD technology employed in the DCVD allowed for not only qualitative study of cooling fuel, but also quantitative description of their Cerenkov glow, assuming reliable baseline information about the assembly. Specifically, this development in Cerenkov viewing gave insights into burnup and cooling time alongside whether an assembly contained irradiated fuel or non-fuel substances.[1] However, the DCVD is not without its downsides, many of which are inherent to its status as an elemental semiconductor, as discussed later in this section.

Spectral Response Issues

Foundational measurements on the intensity of Cherenkov radiation emanating from spent nuclear fuel were performed at the Swedish Central Interim Storage Facility for Spent Nuclear Fuel (CLAB) in Oskarshamn. A specialized spectrometer paired with a photomultiplier tube (PMT) provided preliminary data on the effects of water absorption and optical noise on Cherenkov spectra.[2] Since the DCVD was not yet commercialized, the wavelengths considered spanned the 250 to 350 nm more representative of the CVD’s response spectrum, and absolute sensitivity for the relevant photons was established via a reference diode. Special care was taken to produce field measurements for fuel assemblies at varying depths within the pond and across a range of burnups. Most important to this paper, that study’s reported spectra were produced with and without the contribution of overhead lights. Contrary to expectations, the largest noise from fluorescent facility lighting was not the 313 nm line from Hg-based fixtures, but rather a separate 331 nm peak. In all cases, a cutoff at 300 nm was observed for the Cherenkov spectra, attributed to absorption in water, which was shifted rightward with greater distance between the sample and detector. Otherwise, attenuation by the water yielded an overall inverse square relationship between depth and count rate.

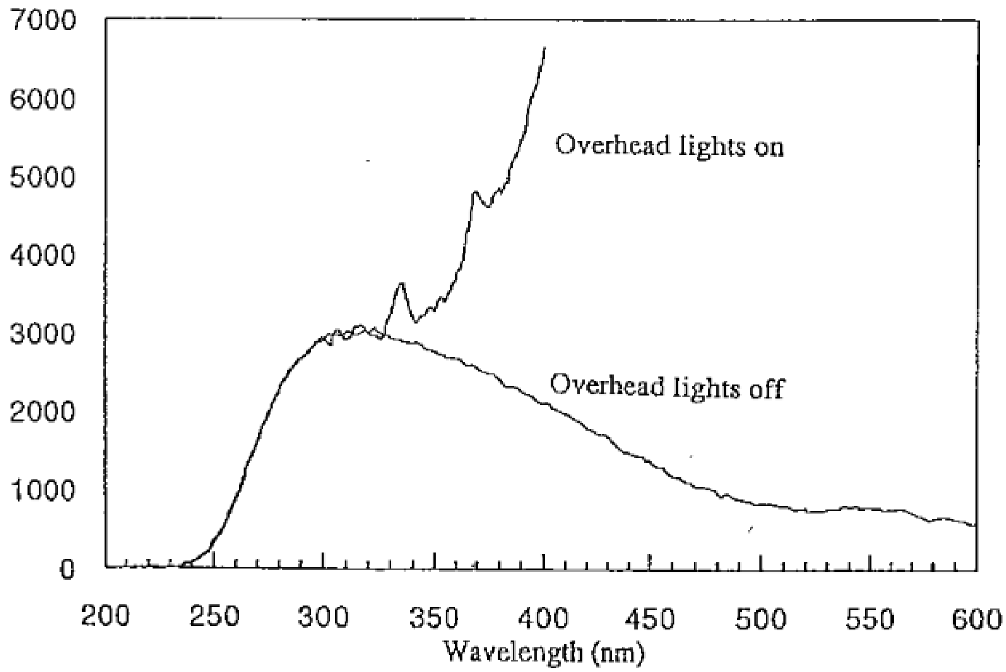

Figure 1. CLAB Measured Impact of Overhead Lighting on Cerenkov Spectrum[2]

In any event, Cerenkov detectors must contend with the noise produced by facility lighting, as operators are unable to turn off lights during inspections for safety reasons. This poses a problem for Si-based devices like the DCVD because of the relatively narrow 1.14 eV bandgap of elemental Si. The magnitude of this value correlates to the detector medium's sensitivity to higher wavelengths of light as well as thermal excitations. Therefore, a narrower wavelength necessarily introduces unwanted lower frequency noise outside of the desired Cerenkov range. To remedy this, the DCVD makes use of an optical filter, allowing for only UV transmission onto the face of the CCD. Unfortunately, while this succeeds in eliminating all but < 0.1 % of photons outside 295-340 nm, it also rejects 20% of the signal within that range, resulting in reduced sensitivity.[3] This problem is almost unavoidable with elemental Si, because, unlike compound semiconductor materials like Ga_2O_3, its bandgap cannot be engineered.

Possible Role of Radiation Hardened Devices

Standard procedure for determining bulk or partial defect of cooling pressurized water reactor (PWR) fuel has heavily relied on an array of specialized devices such as the FORK detector and iterations on the Cerenkov viewing devices such as the Improved Cerenkov Viewing Device (ICVD) and DCVD. The FORK detector, which consists of an ionization chamber for gamma characterization and two neutron-sensitive fission chambers, cannot detect fuel pin diversion with high sensitivity; it only reliably distinguishes a defect case when over half of the assembly is missing.[7] Similarly, existing Cerenkov-based techniques are not foolproof either: weaker light emission due to longer cooling times or high burnups prevents the standard ICVD from verifying partial defect. Although more sophisticated than the standard ICVD, the DCVD also suffers from sensitivity issues that preclude it from distinguishing defects below 50%. This is due to, among other things, obstructions and distortions inherent to viewing the pool from above.[8] Recent simulations show that Cerenkov light spectra cannot be appreciably impacted to improve partial defect detection simply by changing the viewing angle from outside the pool.[9] Some of these limitations of traditional Si Cerenkov detectors serve as the motivation for investigating more radiation-hard wide bandgap alternatives. As such, wide bandgap materials like gallium oxide could conceivably be deployed for solar-blind imaging, even while fully submerged in the spent fuel pool.

Solar-Blind Gallium Oxide UV Detectors

Gallium oxide (Ga_2O_3) is an ultrawide bandgap (UWBG) semiconductor and emerging competitor to commercialized high energy radiation detector materials. Although characterization Ga_2O_3 has been ongoing for many decades, it only recently became the subject of a great volume of concentrated research. Its bandgap affords it the ability to function in hostile environments with high radiation flux and temperature, although its thermal conductivity still lags its UWBG rivals. Across both crystalline polymorphs and its amorphous form, the material benefits from extreme versatility in growth methods while maintaining exceptionally high breakdown voltage, chemical stability, and Baliga's figure of merit (BFOM), a measure of compatibility with power-switching devices. Even more pertinent to this work, Ga_2O_3 has been identified as an outstanding candidate for ultraviolet (UV) light detection for some time. Many devices have been fabricated in laboratory settings to demonstrate the semiconductor's natural propensity to perform well as a visible-blind, and even solar-blind detector.

Ga_2O_3's forbidden band between its electronic states that is far larger than that of even GaN and 4H-SiC, let alone Si, and this bandgap is even broader for the material's α-phase. α-Ga_2O_3 represents one of best candidates for devices that demand high breakdown fields, negligible thermal excitation, and response spectra tailored for specialized roles such as solar blind operation. As a bonus, compound semiconductors like Ga_2O_3 have tunable bandgaps that can further optimize their detection performance. Further distinguishing it from even its wide bandgap counterparts like $Al_xGa_{1-x}N$, ZnMgO, and diamond, Ga_2O_3 suffers from relatively few performance issues following bandgap engineering.[10]

Intense scrutiny has fallen upon Ga_2O_3 devices that can naturally detect wavelengths in the deep UV, potentially offering the desirable feature of solar blindless. In common usage, this term refers to detectors that absorb UV radiation with wavelengths smaller than 280 nm, but remain transparent to lower frequency light. This is mainly useful because UV light above 280 nm almost exclusively becomes absorbed by Earth's ozone layer. Especially at lower altitudes or indoors, the effect becomes even stronger, whereby essentially no cosmic sources of this high frequency UV can contribute to noise. A wealth of solar-blind Ga_2O_3 photodetectors have been reported, many of which have desirable features for Cerenkov-based safeguards, such as avalanche photodiodes and pixelated solar-blind imaging arrays.[10, 11]

Methods

Capitalizing on the many attractive qualities of Ga_2O_3, we seek to develop a solar-blind Ga_2O_3 photodetector specialized for use in Cerenkov-based international safeguards. This means not only fabricating a device with strong response characteristics in the deep UV, but also demonstrating the feasibility of eliminating persistent noise sources such as the 331 nm fluorescent lighting peak through bandgap engineering. To provide partial and bulk defect efficacy, it would be advantageous to develop a pixelated array of photodetectors akin to work performed by Zhou et al. Before creating this more complex architecture, efforts are underway to grow α-Ga_2O_3 crystals through facile mist-CVD methods, thereby demonstrating a cost-effective fabrication method for solar-blind APDs. Using a scratch-built mist-CVD furnace, gallium acetylacetonate precursor and a diluted HCl solution in deionized water is vaporized using an ultrasonic mist generator before being fed into a heated quartz chamber under nitrogen atmosphere. Resting on high-purity quartz boats within the furnace, double-side polished c-plane (0001) Al_2O_3 sapphire crystals are used as substrates for preliminary depositions to test growth parameters. Once calibrated, the mist-CVD furnace will be applied to fabrication of α-Ga_2O_3/ZnO heterojunctions, which will serve as the basis for solar-blind APDs. Crystalline quality of these depositions will be assessed through X-ray diffraction analysis techniques, after which a Schottky contact will be formed on the α-Ga_2O_3 face. Subsequent analysis of absorption spectra will proceed using a spectrophotometer before current-voltage (I-V) and current-time (I-t) measurements will provide initial optoelectronic characterization.

Conclusion

Acknowledging emerging verification issues surrounding bulk and partial defect measurement of LWR spent fuel in cooling pools, preliminary research efforts were performed towards the fabrication of wide bandgap compound semiconductors for Cerenkov detection. Considering the need for a readily tunable bandgap to address certain environmental noise factors such as overhead lighting, Ga_2O_3 is chosen as a promising candidate. Efforts center around mist-CVD growth of the α-phase polymorph for not only its uniquely wide bandgap, but also its low temperature requirements. To produce a photodetector capable of amplifying weak Cerenkov signals, progress is made towards α-Ga_2O_3/ZnO isotype heterostructures grown using a scratch-built furnace. Future work is aimed at bandgap engineering to isolate the 331 nm fluorescent lighting peak, as well as the eventual construction of a pixelated array for Cerenkov imaging purposes.

Acknowledgements

This research was performed under appointment to the Nuclear Nonproliferation International Safeguards Fellowship Program sponsored by the National Nuclear Security Administration's Office of International Nuclear Safeguards (NA-241).

This paper was approved for classification clearance under the number SRNL-STI-2023-00190.

Keywords

ultraviolet, Cerenkov, solar-blind, semiconductor materials, radiation detection, international safeguards, gallium oxide, wide bandgap

References

1. Attas, E. M, Burton, G. R, Chen, J. D, Young, G. J, Hildingsson, L, Trepte, O. 1996. A Nuclear Fuel Verification System Using Digital Imaging of Cherenkov Light, *Nuclear Instruments & Methods in Physics Research A*, Vol. 384, Issue 2-3, pp. 522-530.
2. Ilver, L. 1993. Technical Report on Cherenkov Light Measurements at CLAB, pp. 1-8.
3. https://channelsystems.ca/products/digital-cerenkov-viewing-device-dcvd/dcvd, accessed April 14, 2023.
4. Virgili, N. The Impact of Small Modular Reactors on Nuclear Non-Proliferation and IAEA Safeguards. 2020.
5. Shikha, P, Abdulla, A, Morgan, M. G, Azevedo, I. L. 2015. Nonproliferation Improvements and Challenges Presented by Small Modular Reactors. *Progress in Nuclear Energy* Vol. 80 pp. 102-109.
6. Whitlock, J., Sprinkle, J, 2014. Proliferation Resistance Considerations for Remote Small Modular Reactors. *Nuclear Review* Vol. 1, No. 2, pp. 9-12.
7. Fang, M., Altmann, Y., Della Latta, D. *et* al, 2021. Quantitative Imaging and Automated Fuel Pin Identification for Passive Gamma Emission Tomography. *Sci Rep* **11**, 2442.
8. Branger, E, 2018. Enhancing the performance of the Digital Cherenkov Viewing Device: Detecting partial defects in irradiated nuclear fuel assemblies using Cherenkov light.
9. Branger, E, Elter, Z, Grape, S, Jansson, P, Markus, P, 2021. Combining DCVD Measurements At Different Alignments For Enhanced Partial Defect Detection Performance, *INMM & ESARDA Joint Annual Meeting*.
10. Zhou, Shuren, Zheng, Qiqi, Yu, Chenxi, Huang, Zhiheng, Chen, Lingrui, Zhang, Hong, Li, Honglin, Xiong, Yuanqiang, Kong, Chunyang, Ye, Lijuan, Li, Wanjun. 2022. A High-Performance ε-Ga_2O_3-Based Deep-Ultraviolet Photodetector Array for Solar-Blind Imaging, *Materials*, Vol. 16, No. 1:295.
11. Chen, X., Xu, Y., Zhou, D., Yang, S., Ren, F.F., Lu, H., Tang, K., Gu, S., Zhang, R., Zheng, Y. and Ye, J., 2017. Solar-blind photodetector with high avalanche gains and bias-tunable detecting functionality based on metastable phase α-Ga_2O_3/ZnO isotype heterostructures. ACS applied materials & interfaces, Vol. 9, No. 42, pp.36997-37005.