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# Sustainable Solutions for Gallium and Arsenic Extraction from Semiconductor Industry Waste – A Comprehensive Review

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***Abstract*: Gallium Arsenide (GaAs) is widely used, as a substrate, in the semiconductor industry because of its versatile applications. However, the continuous utilization of this compound has raised many environmental concerns related to GaAs toxicity. During the manufacturing and processing, a tremendous amount of unproductive GaAs is formed, and the wastewater discharged after cleaning the substrate contains both Gallium (Ga) and Arsenic (As) which is hazardous and carcinogenic to the living organisms. This review highlights the environmental challenges associated with the use of GaAs in semiconductor manufacturing and discusses the current advancements and techniques implemented in semiconductor fabrication plants to minimize waste and improve the recovery and recycling of these materials. The review emphasizes the importance of developing sustainable practices to mitigate the environmental impact of semiconductor manufacturing, aiming to enhance industry sustainability by refining recovery processes and reducing the reliance on novel material extraction.**

***Keywords*: Artificial Intelligence, Arsenic, Datacenters, Gallium, GaAs, Recycling, Semiconductor Waste.**

## 1. Introduction

Semiconductors are the essential components of electronic devices and extensively used to fabricate integrated circuits (IC's). Nanotechnology has made revolution in various fields like semiconductors, composite material, supercapacitors, biomedical, water filtration, etc. [1]-[12]. The demand for micro and nanochips contributes to the significant growth of semiconductor industries. Gallium Arsenide (GaAs) is one of the commonly used materials in the fab industry because of its high electron mobility and velocity, direct bandgap, low noise, and faster switching properties than Si [13], [14]. GaAs is a widespread semiconductor for solar cells, supercomputers, field-effect transistors (FETs), electro-optical devices like light-emitting diodes (LEDs) and lasers [15]. Additionally, GaAs has been extensively explored in the development of photodetector devices utilizing nanowires. This research has significantly improved device performance by exploiting the unique properties of nanostructures combined with III-V materials on both Si and Graphene substrates [16]-[20]. This integration capitalizes on the advantageous electronic and optical properties of GaAs, leading to improvements in efficiency and functionality across various applications. Recent advancements have also demonstrated the acceleration of neural network controllers embedded in GaAs-based systems, particularly for solar inverters, using novel dropout techniques to enhance performance and reliability [21], [22]. Moreover, GaAs-based components are crucial in the development of advanced face recognition systems using deep learning, as demonstrated in our research [23], [24].

The use of Gallium Arsenide (GaAs) in semiconductor industries extends beyond traditional devices, finding relevance in high-performance applications such as high-frequency and optoelectronic devices. This is due to its superior thermal stability, high breakdown voltage, and higher electron mobility compared to silicon, making it ideal for devices that require fast-switching speeds and minimal signal loss. The material's applications in military radar, satellite communication, and high-efficiency solar cells have also expanded, reinforcing its critical role in next-generation technologies [25].

Furthermore, with the growing demand for GaAs-based devices, waste management strategies have become crucial, particularly due to the presence of toxic arsenic. During the fabrication of GaAs devices, significant waste is generated, including slurries and particulate matter rich in arsenic, posing environmental and health risks. GaAs processing waste streams often contain high concentrations of arsenic and gallium, which require efficient recycling and recovery processes to minimize environmental impact. Recent advancements in solvent extraction and hydrometallurgical processes have demonstrated high recovery rates of gallium from etching solutions, while also reducing arsenic contamination through precipitation techniques [26].

Additionally, vacuum metallurgy has emerged as a viable method for recovering gallium and separating it from arsenic at lower energy costs, addressing the need for sustainable and economically viable waste treatment solutions [27]. These developments are critical, not only for mitigating the environmental risks of arsenic contamination but also for ensuring a stable supply of gallium for use in gallium nitride

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(GaN) applications, which are vital for power electronics and energy-efficient technologies [28].

Despite a downturn in semiconductor market revenue in 2019 following the COVID-19 pandemic, the sector experienced a robust recovery, with a projected growth of nearly 6% by 2024, spurred primarily by the rollout of 5G technology [29], [30]. IHS Markit technology forecasts that the global revenue of the semiconductor market reached approximately US $448 billion by 2020 [31]. GaAs has been instrumental in this growth, particularly in power amplifiers where its applications in low noise and high gain at very high frequencies are critical [32].

Additionally, Gallium (Ga) is crucial in the production of Gallium Nitride (GaN) Field-Effect Transistors (FETs) and Integrated Circuits (ICs). These components are renowned for their compact size, high switching frequencies, and superior efficiency, addressing key challenges in power delivery architectures. With the escalating demand for computing applications such as cloud computing, machine learning, and artificial intelligence (AI), data centers are expected to consume about 1/10th of the global power [33]. When semiconductor components, such as GaAs and GaN, in data center servers reach the end of their life, recycling is essential due to the toxicity of As and the value of Ga. However, the process is costly and complex, making it less widespread, with the safe handling of As being a significant challenge. Future recycling efforts are focused on developing green chemistry approaches and more efficient techniques for recovering Ga while managing As safely. As awareness of environmental impacts grows, there is increasing emphasis on creating scalable, cost-effective methods for sustainable GaAs and GaN recycling.

While much research has been conducted on nitride wastes [34], [35], this review primarily concentrates on the waste management of Ga and As from GaAs materials, exploring potential treatment and recovery processes applicable to GaN industries as well.

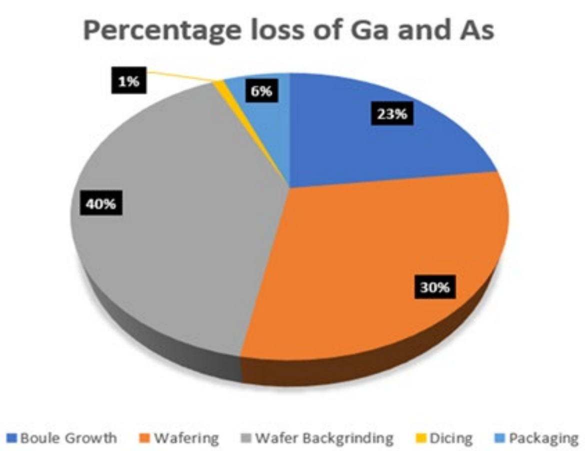


Fig. 1. GaAs loss during processing [14]

GaAs, noted for its softness and brittleness, poses challenges in device fabrication as it is prone to breakage, leading to substantial waste generation during processing. The percentage of waste of GaAs during processing without recycling [14] is shown in figure 1. After wafer processing, surface cleaning is performed using deionized (DI) water which in turn produces waste slurries containing GaAs particulates and liquified arsenic. To increase the thickness during the manufacturing, additional GaAs layers are grown on the wafer which contains a greater volume of pure As than Ga [36]. While the dissolution of GaAs, a large amount of extremely toxic and flammable arsine gas is formed due to a high concentration of arsenic in wastes [37].

## 2. Arsenic Contribution to Wastewater

The presence of As in industrial wastewater is contributed from different processes.

### *A. Grinding*

This process is done to decrease the wafer thickness for stacking and packaging which involves various mechanical wafer handlings such as slicing, wafer back-grinding, and dicing. Grinding contributes to the highest percentage of total GaAs in industrial wastewater. The mechanical abrasion involved in grinding removes substantial amounts of the GaAs substrate, resulting in solid GaAs particles and dissolved arsenic entering the waste stream. These particles are hazardous due to the potential for arsenic to leach into water sources. Studies have shown that grinding slurries contain substantial concentrations of GaAs, with dissolved arsenic levels reaching dangerous concentrations [25]. To address this issue, advanced filtration methods are being explored to reduce the release of these particulates into the environment [26]. During this process, a large amount of substrate is removed and ends up in waste streams as solid GaAs particles and dissolved arsenic.

### *B. Lapping and Etching*

After grinding and slicing, the wafers are lapped to remove the damaged surface. While lapping, atom misplace happens which are treated using wet and dry etching. Wet etching uses acids like nitric, sulfuric, and hydrofluoric acid, contributing to significant arsenic dissolution. This phase of processing produces slurries rich in dissolved arsenic and GaAs particles. The impact of acid etching is particularly severe in terms of arsenic contamination, and advanced chemical treatments are necessary to reduce the environmental footprint of these processes. The efficiency of recovery systems, such as using ferric salts to precipitate arsenic, has been demonstrated to reduce arsenic concentrations in the effluent significantly [28]. Acids such as nitric, sulfuric and hydrofluoric are used to perform wet etching which results in aiding of dissolved arsenic in slurries. The percentage of solid GaAs and dissolved As is shown in Table 1.

### *C. Wafer Thinning and Polishing*

Thinning removes the material from the backside of a wafer, chemically, to preferred thickness. Thinning the wafer involves the removal of material from the backside, often chemically, which leads to the generation of waste containing high levels of dissolved arsenic. Polishing, while necessary to relieve surface stress and damage, further adds to the concentration of dissolved arsenic in wastewater. Recent studies have identified that polishing slurries can have arsenic concentrations as high as 1800-2400 mg/L, far exceeding safe disposal levels. This makes the recovery and treatment of arsenic in these stages critical for compliance with environmental regulations [27]. Methods such as membrane filtration and advanced oxidation processes (AOPs) are being explored to treat this wastewater effectively [25]. Stress and surface damage are treated by polishing. A large amount of dissolve As is contributed during this process.

Table 1
Characteristics of GaAs [14]

| Type | Total GaAs (gram per lt) | pH | Dissolved As (mg per lt) |
|---|---|---|---|
| Grinding slurry | 20-25 | 7.0 | 10 |
| Lapping slurry | 20-30 | 8.0 | 20-90 |
| Polishing slurry | 3-5 | 6.0 | 1800-2400 |

## 3. Gallium Contribution to Wastewater

Gallium is highly soluble at a lower pH level i.e., pH less than 3. As per [37], the solubility decreases as pH level increases from 3 to 4, thereafter it increases proportionally with pH. For a pH level greater than 4, Ga is present in Ga〖(OH)〗_4^- [38]. But, Ga in equilibrium with 〖(OH)〗^- is insoluble because of its low solubility constant. The pH content during polishing is low compared to other processes which means that most of Ga dissolved in fab water is through wafer polishing.

This pH-dependent behavior has significant implications for wastewater management in semiconductor fabs. Processes like wafer polishing, which typically occur at lower pH levels, contribute the largest amount of dissolved gallium to wastewater. Gallium contamination is a growing environmental concern due to its toxicological impacts on aquatic systems. High concentrations of gallium can inhibit plant growth and affect aquatic organisms by altering enzymatic processes and cellular functions [39]. Moreover, the pH of industrial wastewater can fluctuate significantly between processes, further complicating treatment and recovery efforts. For example, in polishing slurries, the concentration of dissolved gallium can exceed 1900 mg/L, making it critical to adjust the pH during treatment to optimize gallium precipitation [26].

The environmental management of gallium requires a multifaceted approach. Wastewater treatment methods such as chemical precipitation, ion exchange, and membrane filtration have been applied to remove gallium effectively. Precipitation with hydroxides can convert dissolved gallium to an insoluble form, while ion exchange resins help capture gallium ions from solutions with varying pH levels [25]. Additionally, electrochemical methods are being explored to enhance the efficiency of gallium recovery from wastewater streams, ensuring both environmental safety and resource reuse.

Wastewater treatment systems must be designed to account for these solubility shifts, ensuring that gallium is effectively removed from both acidic and alkaline waste streams. Continuous monitoring and adjustment of pH levels during processing and treatment can help achieve optimal gallium recovery and reduce the risk of environmental contamination.

Also, a very low amount is dissolved during the grinding process. Even the case study in [15] summarizes that the dissolved As and Ga content in wastewater is high for the polishing slurries which is over 1900 $mgL^{-1}$.

## 4. Environmental Health Effects

Webb et al. in 1984 [39], demonstrated the absorption of GaAs in animal models and epitomized the endanger of airborne GaAs particulates in humans. The study revealed that GaAs inhalation leads to significant lung tissue damage, pulmonary inflammation, and pneumocyte hyperplasia, suggesting severe health risks for those exposed to GaAs particles in industrial settings [39]. Supporting the work of Webb et al., in 1987 National Institute for Occupational Safety and Health (NIOSH) brought the attention of potential risks in workers in the microelectronic industries when associated with GaAs [40], [41]. Accordingly, certain permissible exposure limits (PEL) are established by NIOSH administration. Moreover, the case study in [42] concludes that workers and engineer's health in semiconductor manufacturing industries are badly affected if exposed to higher Ga and As levels and inhalation of As more than allowable limit leads to cancer. Besides, NIOSH recommended the proper use of personal protection equipment (PPE) and clothing. Possible hazards and ways to minimize are shown in table 2.

In humans, ingestion of GaAs causes acute poisoning like vomiting, coma, pulmonary inflammation and pneumocyte hyperplasia, and chronic poisoning which includes anemia, pulmonary lesions, leucopenia and sometimes leads to death [43], [44]. Ingestion of GaAs is equally harmful, with acute poisoning symptoms including vomiting, coma, and pulmonary inflammation. Chronic exposure can cause severe and often irreversible damage, such as pulmonary fibrosis and other respiratory disorders, which may lead to death in extreme cases. These health effects underscore the importance of stringent occupational health and safety regulations in industries that handle GaAs and other hazardous materials.

Long-term exposure to dissolved As in drinking water causes skin lesions, cardiovascular diseases, and diabetes.

## 5. Exposure Limits

The occupational exposure limit for GaAs is 0.002 $mg/m^3$. Whereas for As in the USA is 0.01 mg/m3 (by Occupational Health and Safety Administration) TWA (time-weighted average) and classified as carcinogenic [45]. Short-term exposure limit (STEL) for As measured for 15-min period is 0.002 mg/m3 [42]. The occupational exposure limit (OEL) for Gallium Arsenide (GaAs) is set at 0.002 $mg/m^3$ by various health organizations, including the National Institute for Occupational Safety and Health (NIOSH) and the American Conference of Governmental Industrial Hygienists (ACGIH). This threshold reflects the potential risks posed by inhaling airborne GaAs particles, which have been linked to lung damage and other respiratory issues. Additionally, Gallium Arsenide is classified as a potential carcinogen based on long-term exposure studies [46].

Table 2
Types of semiconductor manufacturing wastes and hazards associated with GaAs processing

| Type of Waste | Associated Risks | Risk Mitigation Practices |
|---|---|---|
| Dust via solid particles | Inhalation of dust | • Implement wet processing techniques to reduce dust creation.<br>• Ensure airflow systems are in place at grinding and sawing stations.<br>• Encase waste in a liquid slurry and store in airtight containers.<br>• Employ PPE such as masks, gloves, and protective suits. |
| Waste from grinding, cutting, and lapping slurries | GaAs ingestion | • Manage and dispose of waste under strict adherence to hazardous waste regulations. |
| | Skin contact, environmental contamination, and arsine gas production from unsafe disposal | • Use protective clothing and gloves consistently.<br>• Avoid conditions that reduce waste slurry, which could release harmful gases. |
| Polishing slurries | Arsenic ingestion | • Protective clothing and gloves should be worn to minimize direct contact with harmful substances. |

For arsenic (As), the Occupational Safety and Health Administration (OSHA) has established a Time-Weighted Average (TWA) exposure limit of 0.01 mg/m³, reflecting the average allowable concentration over an 8-hour workday. Arsenic is classified as a carcinogen due to its strong association with lung, bladder, and skin cancers upon prolonged exposure. In the USA, arsenic is also subject to a Short-Term Exposure Limit (STEL), which is measured over a 15-minute period, set at 0.002 mg/m³ [47].

Moreover, stricter exposure limits have been adopted in other regions. For instance, the European Union's limit for arsenic in the workplace is often set at 0.005 mg/m³ due to its well-documented carcinogenic properties and its prevalence in various industrial settings, particularly in semiconductor and metal refining industries [48].

To mitigate these risks, exposure monitoring and the use of personal protective equipment (PPE), such as respirators and ventilated workstations, are critical in environments where GaAs and arsenic are present. Proper adherence to these limits is essential for minimizing occupational health risks associated with gallium and arsenic exposure.

## 6. Treatment and Recovery Methods of Ga and As

### *A. Treatment and Recovery of As*

There are several methods to treat the dissolved and suspended As in wastewater. When As is dissolved in water, it can exist in either arsenite (As (III)) or arsenate (As(V)) form which is +3 and +5 valence in As atom, respectively. Usually, arsenite is desired in a solution with low redox potential (Eh) and pH whereas arsenate is preferred at high pH and Eh values [49, 50]. The acceptable pH range for drinking water is 6.5 to 8.5. So, to make the fab wastewater to usage needs, firstly the pH must be adjusted to an acceptable range. This is achieved by using sodium hydroxide and/or sulfuric acid. Secondly, maintaining the Eh above 400meV by oxidation to conserve the As in As (V) form using potassium permanganate or metal hydroxide adsorption technique. This is done because As (V) above pH level 2 is anionic and can be removed easily (99.99% free) from water. Thereafter, flocculant, high molecular weight polymer, ferric sulfate or chloride and slaked lime is added to settle down the As at the bottom and then filtration is performed. This is one of the conventional methods to remove the dissolved As from fab water [49]. Moreover, a small amount of As is settled at the bottom which can be removed by a complementary procedure. Bentonite, which is a good adsorbent, is used for the removal of additional settled As and is enhanced by activated carbon and organic adsorbent [51], [52]. The whole process is shown in figure 2.

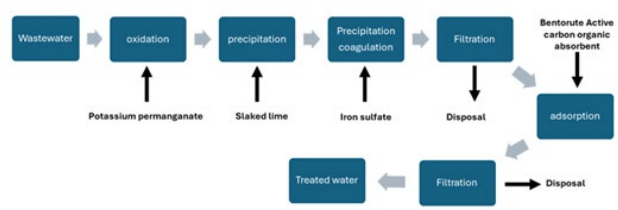


Fig. 2. Treatment of dissolved As

Alternate methods such as reverse osmosis [53], ion exchange using activated alumina or sulfate [54], coagulation [55] with assisted microfiltration, two-stage treatment (FeCl3 and bentonite) [56] and electrodialysis reversal [49] are also performed which were reviewed by Environmental Protection Agency (EPA) and categorized as best available technologies (BAT). Leaching in the nonvolatile ionic liquid is performed to avoid the formation of arsine gas [37], while ion exchange is particularly useful for removing As (V) from wastewater. Coagulation with microfiltration and a two-stage treatment process using $FeCl_3$ and bentonite have been identified as best available technologies (BAT) by the Environmental Protection Agency (EPA). Electrodialysis reversal is another emerging technique, which efficiently separates arsenic ions from water by using an electric potential to drive the ions through semi-permeable membranes [57].

To prevent the formation of hazardous arsine gas during arsenic treatment, non-volatile ionic liquids can be used for leaching, providing a safer alternative for industrial applications where leaching is required [25].

For the suspended As, the centrifugal method is the effective one that has been implemented to remove a large portion of GaAs particulates. Using this process, the particles are collected of which nearly 80 percent are solids and remaining in the form of a paste. Other approaches to eradicate the GaAs particles are enhanced centrifugation and membrane separation [49]. Membrane separation methods, such as ultrafiltration and nanofiltration, are particularly useful for capturing smaller GaAs particulates and suspending arsenic from the wastewater stream [25], [28].

### *B. Treatment and Recovery of Ga*

The percentage of Ga compounds present in the waste streams is insignificant when compared with As. Most of the wastewater in the GaAs industry contains either GaAs particles or dissolved As. Though, there are few methods implemented in the literature to extract Ga from industrial wastewater.

Ga is treated by hydro, pyro or vacuum metallurgy process. The electrolysis method is one of the hydrometallurgy processes, were in Ga is recovered by nitric acid decomposition and sulfide precipitation. Pyrometallurgy process makes use of chlorine and vacuum distillation process. The vacuum thermal decomposition method is a vacuum metallurgy process that effectively recovers Ga, 99 percent pure, with minor lost percent. Distillation temperature and time are the main factor of this process [58], [59].

In addition to these conventional methods, solvent extraction techniques have been explored as an effective means to separate gallium from acidic solutions. Studies using Cyanex 272 and other organophosphorus-based solvents show high efficiency in gallium recovery, especially from GaAs waste etching solutions, with extraction rates exceeding 95%. These methods are particularly useful in combination with pH control, allowing gallium to be recovered selectively from complex waste streams [26].

Another emerging approach is biosorption, where microorganisms like bacteria or algae are used to adsorb gallium from wastewater. Recent studies demonstrate that freshwater green algae (Chlorella sorokiniana) shows a high adsorption capacity for gallium, even at low pH levels [60], [61]. This method presents a sustainable, low-cost alternative for gallium recovery, with significant potential for scalability in industrial applications. Innovations in nanomaterial-based adsorbents, such as graphene oxide and functionalized silica gels, are also gaining attention for their high gallium adsorption capacity, making them effective for treating gallium-contaminated wastewater [60], [61].

## 7. Disposal Procedures

The discarded GaAs products or the unused wastes are disposed of by landfilling of the residuals after incineration or directly in landfills. But the burning of waste GaAs develops arsenic emissions into the environment which leads to health effects. In [15] suggested that direct landfilling of GaAs industrial waste is the better option than incinerating it.

## 8. Discussion

The major percentage of material present in fab wastewater is As, which has various health effects, so removing As is the important task. Mostly, the traditional method is implemented but as discussed earlier, it has limitations that were unable to meet the current restrictions. Though the substitutional methods are expensive, they are reliable for extracting or eliminating the low concentration As. As per the literature review, reverse osmosis is one of the alternate methods that can be an apt replacement for the traditional method as it is a bit cost-effective and more than 95% of As is been treated and restricts its percentage to present-day limits i.e., 0.01 mg/m3 provided by the Occupational Health and Safety Administration. Apart from solid and dissolved As, arsine gas is also formed which is due to combustion and can cause severe (level 4) health problems. The fab industry such as light-emitting diode manufactures possesses a combustion process, so simple leaching and stripping mechanisms using sodium hydroxide and brominating could be implemented for avoiding arsine gas formation. Moreover, this method is safer and can also extract some crucial metals like iron and copper.

## 9. Conclusion

For removing the As and Ga from semiconductor wastewater accumulated from cutting, etching and cleaning process, different methods were proposed. Recycling helps to recollect more than 50 percent of GaAs particles but for the dissolved As traditional treatment will be incapable because of the rapid growth in technology and change in discharge limits in As. To meet the present-day requirements and restrictions, alternate methods are implemented which are superior over the traditional method. Moreover, the algae-based method to remove Ga from wastewater is the preferable one because it has high adsorption even at low pH values with 99.99% purity.

In the literature, none of the paper has suggested eliminating both As and Ga in a single process. Moreover, using separate methods for detaching individual material is an expensive process. As per my analysis, reverse osmosis followed by simple leaching, for the most part, could eliminate As present in the three forms i.e., solid, liquid and gaseous. Adding a Chlorella sorokiniana absorbent after the coagulation process in reverse osmosis method could extract both Ga and As in a single step. While the coagulation process eliminates the As, the absorbent removes a most percentage of Ga providing Ga free water. To have a further enhancement in controlling the As and Ga in fab wastewater, there should be a trail of the above process and can observe the percentage of As and Ga in the final step.

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