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Freiberger's comments to the ECHA consultation on the 6th priority list of substances for inclusion in Annex XIV

- Comment for diboron trioxide -

CAS Number: 1303-86-2
EC Number: 215-125-8

Position of Freiberger

Freiberger Compound Materials GmbH is located in the Eastern part of Germany. We are the main producer of gallium arsenide (one of only two existing companies) in the entire European Union. Freiberger is the market leader in the field of wireless applications with a market share of about 50%. To defend this position it is a hard and continuous competition with big enterprises producing in Asia like e.g. Sumitomo.

GaAs is the substrate material used in a very complex supply chain around the world for the manufacturing of electronic and photonic devices with very high relevance for the society as well as for consumer articles used in daily life e.g. smartphones, computers, GPS systems, lasers, diodes, solar applications.

GaAs cannot be found naturally. It has to be produced from the ultra-pure raw materials arsenic and gallium. Since the chemical reaction - first to a multi-crystalline material, in a following step to mono-crystalline ingot - requires high temperatures the melt must be covered by a flux to ensure the correct targeted stoichiometry. The substance used for this purpose is diboron trioxide. So the conclusion is easy:

No diboron trioxide – no gallium arsenide production in Europe.

From our perspective an inclusion of diboron trioxide for the special and limited use in semiconductor industry would not be the appropriate option for further regulation beside the already existing legislation.

Arguments and Rationale

Improbability of reproductive and developmental effects in humans caused by borates

Although reproductive and developmental effects have been demonstrated in laboratory animals exposed to abnormally high doses of boric acid, similar effects have not been observed in highly exposed human populations or workers. The absence of adverse reproductive effects in extensive investigations of borate workers in the United States, Turkey and China chronically exposed to high levels of borates and in populations living in high boron areas demonstrate that the actual health risk from exposure to borates is small. Workers in boron mining and processing industries represent the maximum possible human exposure. Based on the total weight of evidence that includes worker exposure data, epidemiological studies and mechanistic data, the data show that it is improbable that boric acid will cause reproductive or developmental effects in humans.

This statement made for boric acid is relevant and applicable as well for diboron trioxide since for this toxicological classification read-across principle was applied. This is known by ECHA.

Use of diboron trioxide at Freiberger

Freiberger uses the diboron trioxide for the manufacturing of gallium arsenide. The substance is supplied as a solid cylinder. Due to their hygroscopic properties the parts are packed into evacuated bags.

Starting with the raw materials arsenic metal and gallium metal the first step is the synthesis of multi-crystalline gallium arsenide. The chemical reaction in a closed system needs high temperatures and pressure. To avoid the outgassing of arsenic the melt is covered by diboron trioxide which is liquid at this stage, too. A chemical reaction between gallium arsenide and diboron trioxide does not happen at any time.

After cooling down both substances are solid again. The multi-crystalline gallium arsenide is separated manually from the diboron trioxide.

During the following single crystal growing process the diboron trioxide is used again as a flux to cover the melt. The solid materials are separated manually as well.

All diboron trioxide is collected very carefully and given into a special developed recuperation process. Used several times for the above described purpose this material finally ends up in the waste stream (see flow chart in figure 1).

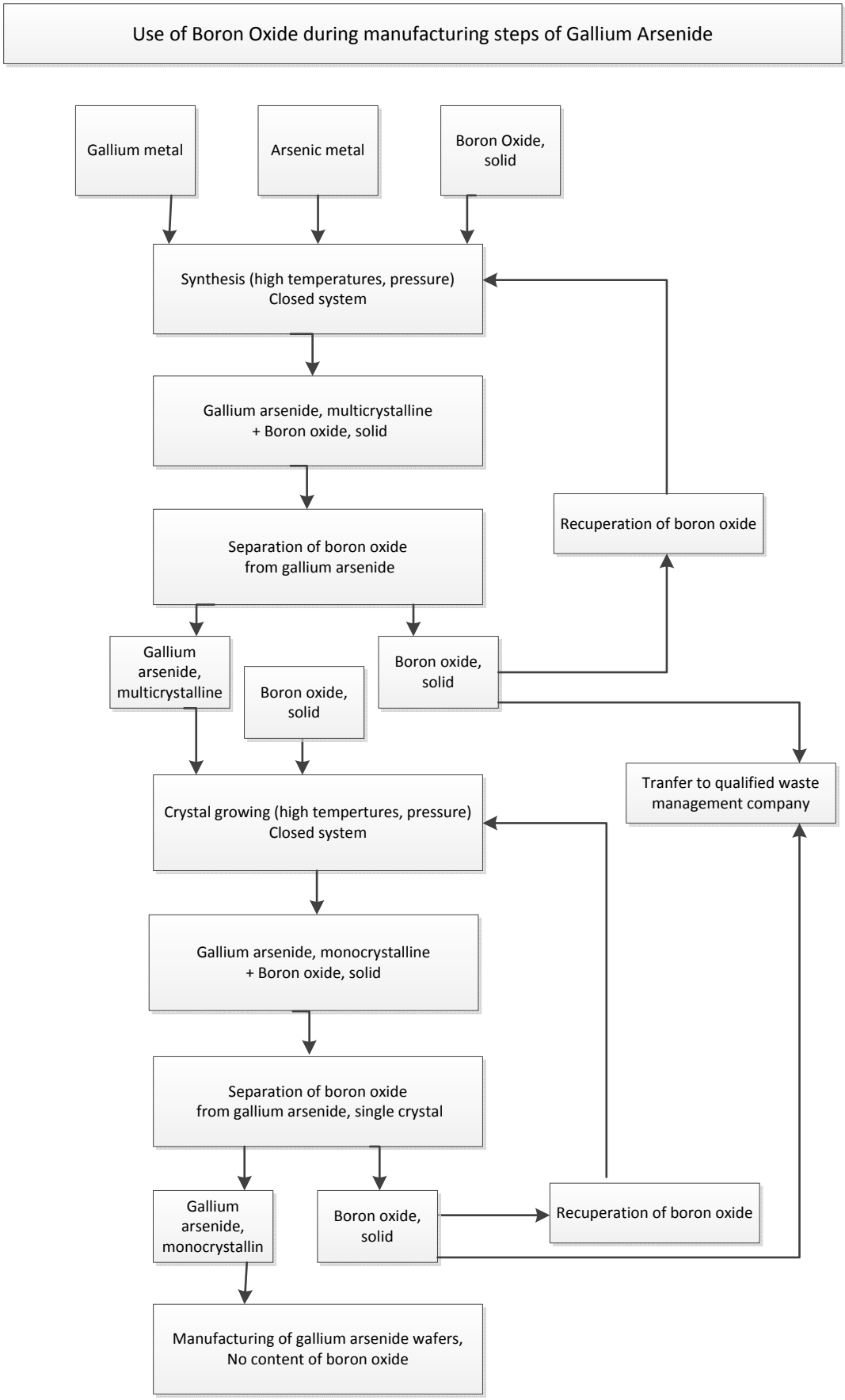

Figure 1: Flow chart for the use of diboron trioxide at Freiberger

Risk related to diboron trioxide and workers protection

Figure 2: diboron trioxide cylinder as supplied in a vacuum-sealed packaging

Diboron trioxide is handled very carefully to protect the quality of this substance and to ensure the appropriate use in our processes. All workers are skilled and regularly trained according to the actual legislation. Related risk management measures are in place. The real exposure on workplaces was measured by an accredited institution. The values are near or below the detection limit as shown in table 1.

Area at Freiberger	**Risk related to diboron trioxide**	**Duration of possible exposure**	**Measured value of inhalable dust on the working place**	**Risk management measures**	
				to protect the workers	**to ensure quality of used material**
Incoming department and inventory	none, substance is packed in closed, evacuated envelopes	none	none	none	visual inspection of packaging
Synthesis of multi-crystalline GaAs	none, closed system	none	none	closed system	Surgical mask, gloves for removal from packaging and placing on the material

Separation of B_2O_3 and GaAs after synthesis	manual removal of diboron trioxide from the gallium arsenide	max. 2 ½ h per day	0,02 mg/m^3	respiratory mask with filter P3, safety goggles, gloves, special working coats	local exhaust ventilation, wet process,
Single crystal growth	none, closed system	none	none	none	Surgical mask, gloves for removal from packaging and placing on the material
Separation of B_2O_3 and GaAs after single crystal growth	manual removal of diboron trioxide from the gallium arsenide	max. 2 ½ h per day	0,02 mg/m^3	respiratory mask with filter P3, safety goggles, gloves, special working coats	local exhaust ventilation, wet process,
Recuperation of B_2O_3	Selection of gallium arsenide fragments from diboron trioxide	180 min within 4 weeks	< 0,015 mg/m^3	gloves, safety goggles, special working coats	local exhaust ventilation
Transfer to qualified waste management company	load of vehicle transporting hazardous goods	none	No measurements necessary	closed containers	closed containers

Table 1: overview about the working places where diboron trioxide is handled, related exposure data and risk management measures for product quality and workers

As demonstrated in the registration dossier of diboron trioxide a Risk Characterization Ratio (RCR) < 1 was determined. The use and the handling of diboron trioxide to cover the melt of a semiconducting material are already today compliant with the requirements of the REACh regulation to ensure an adequately controlled risk for workers and to design safe working places.

Volume used at Freiberger

In average Freiberger uses a quantity of about 11 t/y diboron trioxide. To save resources a certain amount of this material is recycled internally and used several times in a circular flow. This means that only a percentage of the mentioned quantity is newly supplied every year. Compared with very hazardous substances used > 1000 t/y in the chemical industry this is not much for an industrial use only.

Statement on possible alternatives

Diboron oxide is used in ultra-pure quality and as a massive cylinder (see fig. 2 above) for the synthesis and single crystal growth for several III-V-compounds in semiconductor industry. Its use aims to avoid the outgassing of the component with the lower vapor pressure from the melt. Since this process is running at temperatures about 1000 °C the diboron trioxide becomes liquid, too (see fig. 3, fig. 4 and fig. 5).

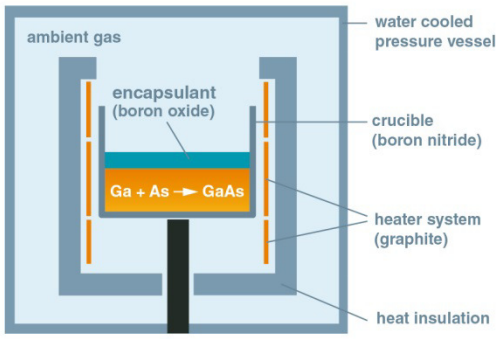

Figure 3: principle of GaAs synthesis

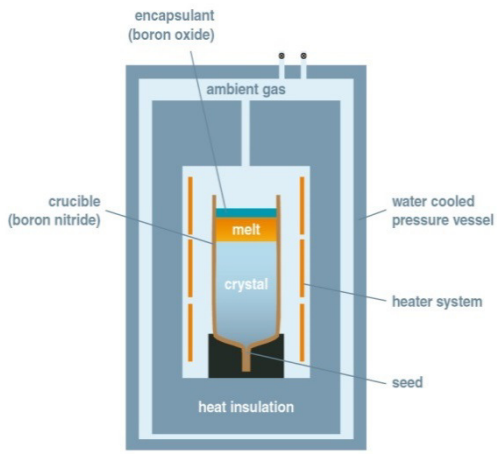

Figure 4: principle of VGF crystal growth

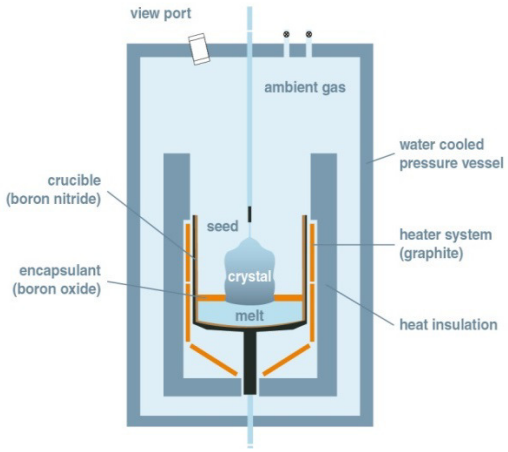

Figure 5: principle of LEC crystal growth

This layer of diboron trioxide features unique properties e.g. low density, extreme low level of metallic impurities and controlled water content which are absolutely necessary to adjust and ensure the semiconductor quality of the manufactured compounds.

Although several technologies for the production of semiconductor materials have been developed and improved globally in the past 50 years there is no alternative substance/mixture for this purpose. Detailed explanation is given in the attachment to this comment.

Proportionality and effectiveness of regulatory instruments

During the last years the EU officially implements the SVHC-Roadmap. It contains a very strong tool to screen and analyze the different categories of SVHCs – the Risk Management Option Analysis (RMO-A). In 2013 it was stated by the EU COM that there is a need to consider reasons for not wanting substitution of a SVHC at an early stage:

- Economic consequences
- Societal key function
- Environmental benefit

Member States, the Commission and ECHA agreed already in January 2009 to carry out the RMO analyses in order to:

- support the decision-making on which risk management route should be followed

and

- share the conclusions with all parties **before** submitting Annex XV dossiers.

To our knowledge for diboron trioxide such a RMO-A has not been carried out. So we would like strongly recommend this assessment in order to achieve the best RMM option for diboron trioxide.

For the use of mixtures containing diboron trioxide a Specific Concentration Limit of c ≥ 3.1% (w/w) is applied. Therefore by applying the read-across principle also for the use of diboron trioxide as flux for a melt in the semiconductor industry a similar Specific Concentration Limit (SCL) seems to be the appropriate measure due to the following facts:

- very special industrial use of diboron trioxide only, definitely no consumer exposure
- any possible exposure might occur only to a certain very low and known number of workers within the entire EU
- limited risk is already now adequately controlled for safe working places as described in the registration dossier of diboron trioxide
- handling of a very low quantity of ca. 11 t/y compared to very hazardous substances with tonnages > 1000 t/y e.g. hydrofluoric acid

Assessing these issues and expressing them in a scoring table the result for diboron trioxide is summarized as shown in table 2:

Inherent Properties	Volume	Wide dispersive use
Classified reprotox. cat. 1b (Article 57(b) REACh)	10 – 100 t/y	Industrial use only, no content in articles
Score: 1	Score: 6	Score: 5

Table 2: Freiberger's scoring for its special use of diboron trioxide based on ECHA's document "Prioritisation of substances of very high concern (SVHCs) for inclusion in the Authorisation List (Annex XIV)" dated 10 February 2014

Freiberger's total score = 1 + 6 + 5 = 12

For this use in semiconductor industry this is much lower than ECHA's scoring in the background document (total score 22). Conclusively the score of 12 gives not enough justification to apply an authorization procedure for further regulation in this use.

The authorization should be a proportional procedure. Therefore the scoring system for prioritization was established and gives a ranking for the substances to be regulated. As long as the authorities did not decide exclusively on the 5th list for prioritization the regulation of the substances on the 6th list does not seem being proportional as the substances on the 5th list have presumably a higher scoring.

Conclusion

For the handling of diboron trioxide used in semiconductor industry as described above already now appropriate risk management measures are in place and effective based on the actual legislation. Therefore an authorization would not bring additional value or more protection to the safety and health of humans and environment. The Personal Protective Equipment is not really needed for safety reasons for the workers but much more to ensure the quality of our products.

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