LAYMAN REPORT

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Surface Treatment of Molybdenum Pins to Reduce the Molybdenum Load of the Waste Water

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Summary

In the electronic industry processes, which are necessary for cleaning and etching, cause considerable contribution to environmental pollution. Currently these processes are necessary to remove films of oxide, which would otherwise interfere with the following soldering process in a negative way.

The main goal of the project was to replace the etching process, which was necessary to remove the oxide film on the surface of the Molybdenum pins (Mo pins), by an alternative process of soldering, which had already been developed in the laboratory. The Mo pins are soldered on the nailhead wires of the diodes, which consist of copper.

First of all the oxide film on the Molybdenum pins will be removed at the manufacturers production line by barrel-polishing (Company: Plansee, Tyrol). This is a mechanical process, where the oxides are removed by shearing forces. After this process the pins are put into an air-sealed packing to avoid new oxidation of the surface. At Vishay's the pins are pre-soldered with a new soldering process. The solder, which was selected after several calculations and tests, meets in combination with the new soldering process the very high demands on quality of the customers. Further demands occurred during the projects running period (the so called "Pressure Cooker Test").
Thereby the building of a furnace prototype was necessary to achieve exact temperature control and to control the protective gas mixture. This gas mixture consists of N_2 (for protection) and H_2 (for reduction of oxides on the surface).

The environmental advantages, which are the results of the implementation of the new soldering process, are the reduction of the Mo in the waste water from 18 mg/l down to at least 0.6 mg/l (at full production capacity). This causes a yearly reduction of Mo output into the local river (Vöckla) of 522 kg at full production capacity. This reduction is not only a local effect. Due to the distribution of the Mo over all the following rivers (which finally lead into the Danube) this reduction causes a direct positive impact to other European countries.

Furthermore the implementation of the new process brought a reduction of costs of production and can easily be set up at other production sites.

1. Background and Problem Description

In the electronic industry processes, which are necessary for cleaning and etching, cause considerable contribution to environmental pollution. Currently these processes are necessary to remove films of oxide, which will interfere with the following soldering process in a negative way. The result is a pollution of the body of water (mainly rivers) with heavy metals.

Vishay produces 150 million diodes a year at the production site in Vöcklabruck. These diodes are used for rectifiers or Zener diodes in monitors, switching power packs or discharge tubes. The very high quality and specific properties of the diodes make them competitive against products from far east or other countries with lower wage costs.

During the production process sintered Molybdenum pins (Mo pins) are etched with nitric acid, sulphuric acid and hydrochloric acid to remove the oxide film on the surface and to prepare the pins for the following soldering process. The resulting waste water, which contains 18 mg/l Mo, is passed into the near river Vöckla.

This etching process will be replaced by a process of pre-soldering of the contact surfaces. A solder, which is qualified for industrial production, shall be calculated, tested and implemented in the production process during the projects period. For this production step, already in the laboratory tested processes had to be adapted and prepared for the high number of pieces. Furthermore a furnace prototype had to be build and started to implement the laboratory processes into the industrial production environment.

The superset goal of the project was the reduction of the Mo in the waste water from 18 mg/l down to values lower than 2 mg/l. A total reduction of the Mo was not practicable, because out of another step of the Si-chip production 0.6 mg/l Mo arise and cannot be remove until now.

2. Solutions and Results

As shown in figure 1 a glass bead diode consists of Mo pins, which are soldered to the nailhead wire made of Copper. The Si chip is alloyed with the Mo pins. Finally, after the soldering step and the alloying step, the nailhead wires are tinned.

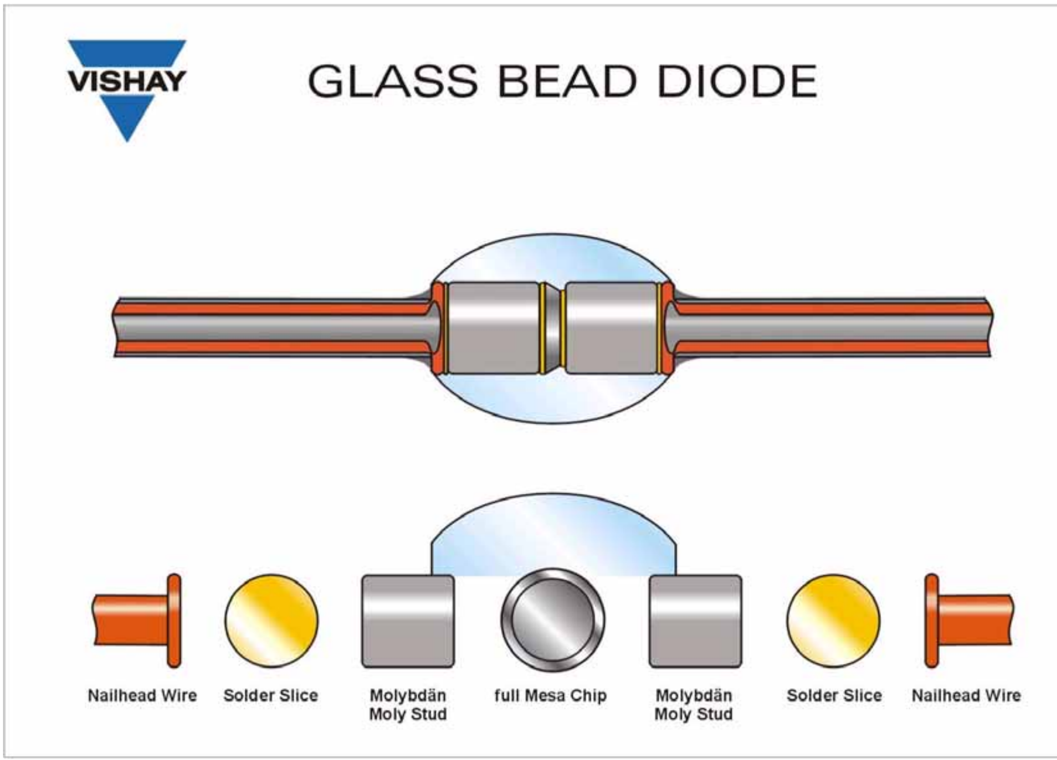

Fig. 1: Components of a glass bead diode. The Mo pins are soldered on the nailhead wires (Copper). Afterwards the Mo pins are alloyed with the Si chip. Finally the diode is covered with a glass paste and sintered.

In figure 2 and 3 scans of diodes made with a scanning electron microscope (SEM) are shown. The position of the alloy of the Si chip with the Mo pins can be clearly seen in figure 2. In figure 3 the soldering joint (Mo pins to nailhead wire) is well visible.

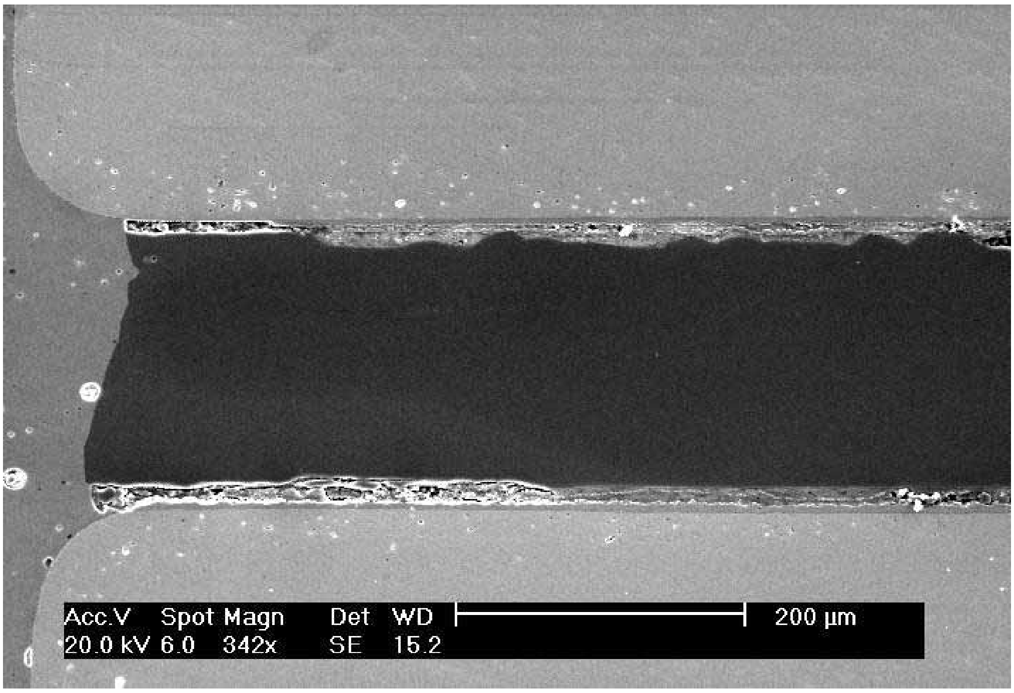

Fig. 2: SEM scan of the Si chip (dark area in the middle of the picture) alloyed to the Mo pins (grey shaded areas at top and bottom)

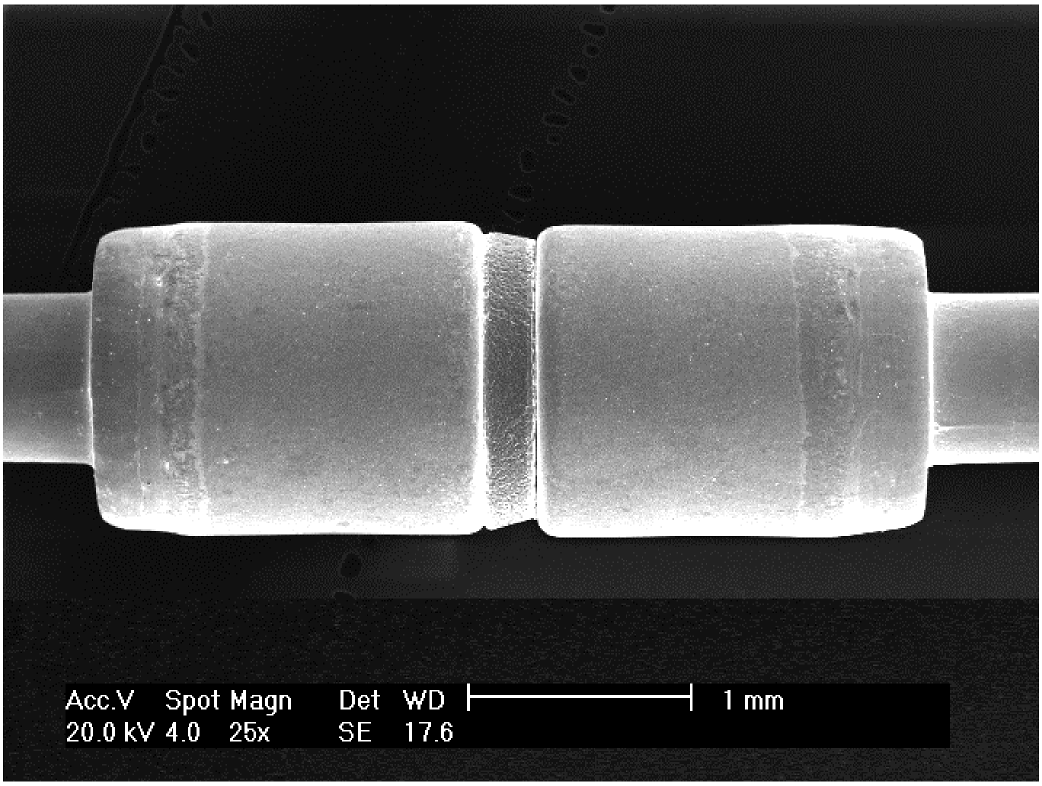

Fig. 3: SEM scan of a diode (without sintered glass). In the middle of the picture the Si chip can be seen (vertical). On the left and the right side the two nailhead wires are visible.

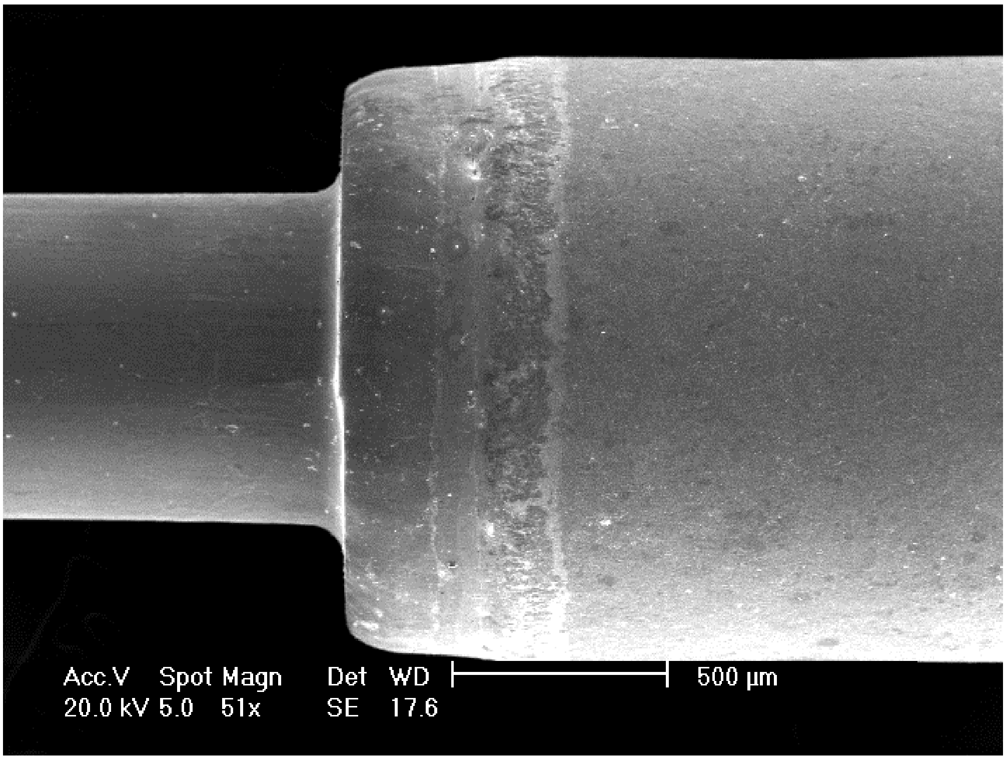

Fig. 4: Soldering joint of the Mo pin and the nailhead wire.

As mentioned in Chapter 1 there exists a very stable oxide film on the surface of the Mo pins, which prevents good and stable soldering. The state of the art to remove these oxide films is etching the surfaces with acids. Thereby the waste water is loaded with Mo.
For the removal of the oxide films without an etching process (as proposed in this project) and to reach a good and stable soldering of the Mo pins, a process, which was developed and tested in the laboratory, was transferred to industrial production conditions during this project. Thereby a pre-soldering of the Mo pins was implemented and a reducing atmosphere (H_2 gas) was used to avoid new oxidation of the oxide free surface and, if applicable, to reduce remaining oxides. The initial removal of the oxide films was done at the manufacturer of the Mo pins (Company: Plansee, Tyrol) by barrel-polishing. Afterwards the Mo pins were packed into air sealed containers to avoid new oxidation.
With this pre-treatment it was possible (by using the appropriate solder) to solder the Mo pins on the nailhead wires and to tin the wires after this soldering.
For the transfer of the laboratory process (soldering and alloying) it was necessary to build a furnace prototype, which had to fulfil the following demands:

- Several zones of temperature to set and control a necessary profile of temperature
- Zones, which provide reducing conditions (H_2 gas) and which allow an adjustable mixture of H_2 and N_2
- Adjustable speed of the conveying belt
- Adjustable cooling down profile

Building of the furnace prototype

During the first half of the project this prototype was specified, built and accepted. The built prototype is shown in figure 5.

Fig. 5: Furnace prototype. In the foreground the conveying belt, which transports the diodes in the carbon container, is visible. On the top (right hand side) of the picture the safety contrivance, which burns emergent H_2 gas to avoid dangerous concentrations of H_2 in the production hall, is shown.

The perfect control of the temperature is necessary, because the soldering process is only operable in a very narrow temperature range. The components of the diodes are put into carbon containers and get soldered and alloyed in the furnace.

Selection of a suitable solder

During the second half of the project the main tasks were the calculations and the tests of a suitable solder. Thereby the demands on the soldering of the customers changed during the project, what is very common in the industrial daily routine. On the one hand the process temperature had to be lowered and on the other hand the diodes had to pass the so called "Pressure Cooker Test".
These changes required the calculations and testing of several solders.
Additionally during the second half of the project it figured out that the use of pure tin (without lead), which is used for tinning the nailhead wires, will be demanded by law in several years. Therefore on the one hand the composition of the solder had to be changed and on the other hand the soldering process had to be modified to reach this demanded tinning with pure tin. This lead-up for the pure tin process requires a short washing step of the Mo pins right before the soldering process. This causes a minimal load of the waste water with 0.6 mg/l Mo at full production capacity.
Thus the total elimination of Mo load in the waste water was not reached fully. But the reduction from 18 mg/l (value right before the beginning of the project) down to 0.6 mg/l (1/30 of the original value) is very noteworthy and an important step to prevent our all environment from pollution with heavy metals.

Changes of the sintered glass

Due to the changes of the soldering process (Mo pin to nailhead wire) and the alloying process (Si chip with Mo pins) on the one hand and the new preparation step of the Mo pins (no etching) on the other hand the glass paste composition had to be changed. These changes of the sintered glass provide a hermetic seal as shown in figure 1.

Transfer of the results

The results achieved in this project will be implemented in a first step into the production line in the Hungarian factory of Vishay. This will cause a significant reduction of the Mo pollution too and it is expected that there will not occur many problems during the set up of the process.

3. Environmental and Economical Advantages

Environmental advantages

As demonstrated in figure 6 the transfer of the process, which was developed and tested in the laboratory, to the industrial production process caused a significant reduction in Mo load of the waste water. In absolute values the load of Mo was reduced from 18 mg/l down to 0.9 mg/l at full production capacity. The additional 0.3 mg/l Mo are the result of an other production step of the glass bead diode. But this step was not part of this project and therefore the contribution to the Mo load out of this step is the same as before the beginning of the project.

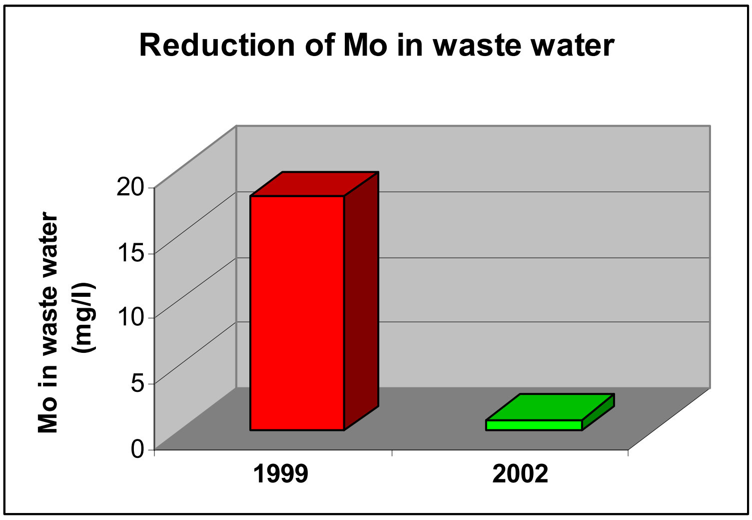

Fig.6: Reduction of the Mo load of the waste water at the beginning of the project in 1999 and at the end in 2002.

Therefore the total Mo load per year is reduced from 540 kg/a down to 18 kg/a at full production capacity (see figure 7).

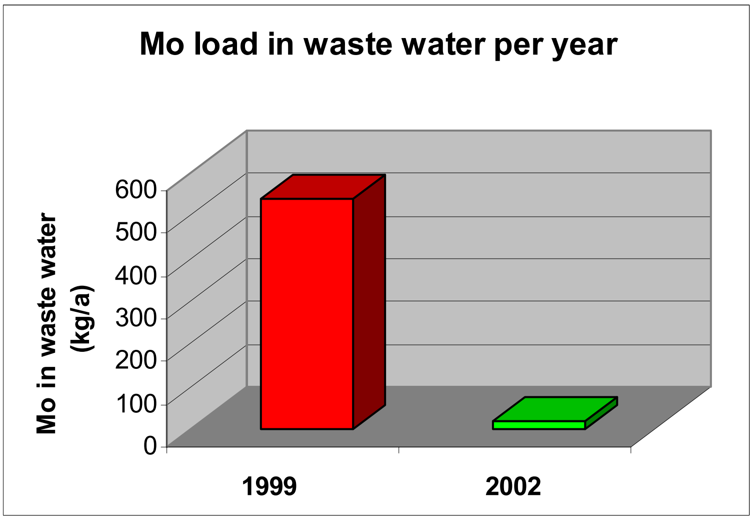

Fig. 7: Reduction of the Mo load in the waste water per year at full production capacity

The reason why a total elimination of the Mo in wastewater was not obtained over the whole production cycle is that there is another production step (preparation step of the Si chip), which leads to 0.3 mg/l Mo load in the waste water at full production capacity. This step was not part of this project. Furthermore a short washing step of the Mo pins is necessary, because of the preparations for pure tin tinning in a few years. This step causes 0.6 mg/l Mo load in the waste water at full production capacity.

Another environmental advantage is the reduction of energy consumption because of the reduction of rejected diodes. This is obtained because of an improved process control in the furnace prototype.

Economic advantages

The economic advantages can be summarised as follows:

- Reduction of contaminated waste water and therefore reduction of costs for waste water treatment
- Reduction of acids used for etching. This causes reduction of costs for the production of the diodes
- Reduction of the number of rejected diodes and therefore increase of productivity

Summing up the improvements obtained for environment cause remarkable economic advantages. The transfer of the processes, which were developed and tested in the laboratory, to the industrial production line contributes in a very positive way to increase the environmental friendliness and to increase the competitiveness of European production.

4. Dissemination of Results

Dissemination of results and the information of the public can be summarised as follows:

- At the beginning of the project a description of the project was sent to the press and the goals were presented.
- Information was given continually to regional and national printing media. Thereby the public were informed about the current state of development and research.

- The employees of Vishay were informed in a separate way via Vishay's intranet. Thereby all employees worldwide got access to the contents of the project and could read all new and current results of the activities.
- At the sites of Vishay charts and pictures, which demonstrated the content of the project, were set up and accessible all the time for employees as well as for visitors. Furthermore references were given, where interested visitors can get more information about the project and its status.
- Information was given to Vishay's customers as quick as possible about new developments and changes. The formally demanded criteria were met.
- Production of an image folder describing the project.