Electron-beam Deposition with Low- Spitting Platinum Source Material Improved by New Impurity Removal Processes

Atsushi Kawashimo[1], Takahiro Kobayashi[1], Masatoshi Koyama[2], Yuichiro Shindo[1]

[1]Technical Development Division, Matsuda Sangyo Co., Ltd.
Shinjuku Nomura Building 6th Fl., 1-26-2 Nishishinjuku, Shinjuku-ku, Tokyo 163-0558, Japan
kawashimo-a@matsuda-sangyo.co.jp, Tel: +81-3-3346-2319
[2]Nanomaterials Microdevices Research Center, Osaka Institute of Technology
5-16-1 Omiya, Asahi-ku, Osaka 535-8585, Japan

Keywords: Precious metals, E-beam evaporation, EB deposition, Pt slugs, Pt nodules, Spitting

Abstract

The generation of metal nodules during electron-beam (EB) evaporation is a serious issue that reduces the wafer yield. During Au thin-film evaporation, Au nodules are produced by the carbon contaminants in the Au slugs used as the evaporation source. In this work, we present a new material-processing technique to reduce the carbon contaminants in Pt slugs, thereby suppressing Pt nodule generation. We suggest adding a new impurity-removal process in the rolling and swaging steps and a new degassing process after the cutting step to reduce the entrapped contaminants in Pt slugs. This new impurity-removal and degassing process can effectively reduce not only carbon contaminants but also other impurities such as Fe and oxygen. By applying this new process to Pt slugs used in EB evaporation, the average number of particles on the Pt thin film can be significantly reduced, to approximately one-seventh of that of the conventional process. The use of low-contamination Pt slugs in Pt thin films produces specific electrical resistivities lower than obtained when using conventional Pt slugs. These results indicate the effectiveness of the new impurity-removal and degassing process in the manufacture of Pt sources exhibiting suppressed Pt-nodule generation during EB evaporation.

INTRODUCTION

Electron-beam (EB) evaporation is typically used in compound-semiconductor electronic and optical-device manufacturing to deposit metal-electrode wiring layers containing high-melting-point metals. In compound-semiconductor devices, the Pt layers formed by EB evaporation are used as Schottky contacts and metal-mixing barrier layers. During the Pt-metal evaporation processes of heating, melting, and deposition via EB irradiation, ballistic Pt nodules generated by the spitting of molten Pt in the source crucible splash from its surface to the substrates. This can reduce the wafer-production yield owing to Pt-nodule–related defects. In the case of Au evaporation, the origin of these nodules is considered to be the carbon contamination in the slug- or wire-shaped raw materials[1].

Although these source metals are mostly certified to exhibit a purity of 99.99% (4N) or higher, the contamination of mechanically formed slugs and wires during the refining and mechanical-forming processes is unavoidable. Carbon crucibles are one such source of carbon contaminants. The lubricants used in the mechanical-forming steps may also lodge in the scratches and crevices on the surface, acting as another contamination source [1]. We developed a new material-processing method to reduce carbon contaminants in Au slugs and verified that their reduction could decrease the short thermal ballistic spitting events[2]. In this study, we propose a new impurity-removal process for the rolling and swaging steps and a new degassing process to be implemented after the cutting step to reduce the entrapped contaminants in Pt slugs. We also clarify the relationship between Pt slug contamination and the generation of Pt nodules during EB evaporation.

EXPERIMENTAL PROCEDURE

Figure 1 shows the manufacturing-process flowcharts for forming Pt slugs by the conventional and newly proposed processes; the Pt slug samples formed by these process are named “Conventional-Pt” and “Improved-Pt” samples, respectively. As shown in Figure 1, a typical manufacturing process for slug-shaped metal sources involves melting raw Pt metal in a carbon crucible, followed by rolling, swaging, cutting, and cleaning the ingot to form barrel-shaped slugs. We developed two different contaminant-removal processes to improve the Pt content. One is a new process to be implemented during the rolling/swaging steps and the other is a new degassing process, which is a modified MNS (Matsuda New evaporation materials for Spitting reduction) treatment[2], to be implemented after the cutting process.

The surfaces of the Conventional-Pt and Improved-Pt slugs were observed using field-emission scanning electron microscopy (FE-SEM, JSM-7000F, JEOL Ltd.) and energy-dispersive X-ray spectroscopy (EDS, Aztec Advanced Ultim Max40, Oxford Instruments) to evaluate the carbon contamination on the surfaces. The oxygen contents of both Pt samples were measured via instrumental gas analysis (external analysis with HORIBA, EMIA 920V). To compare the number of Pt nodules on the evaporated Pt thin films, 100 nm thick Pt thin films were deposited on 100 mm φ Si wafers using an EB evaporator (SIP-700, Showa Vacuum). The deposition rate was set as 1.5 Å/s. Before Pt thin-film deposition, a 10 nm thick Ti layer was deposited as an adhesion layer. A defect/particle inspection system (HYBRID C3, Lasertec) was used to measure the number of particles on the wafers. The resistivities of the deposited films were measured using the four-point probe method (Loresta-AX MCP-T700, Nittoseiko Analytech).

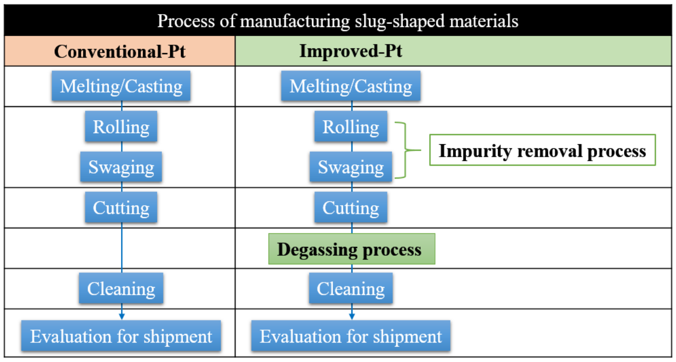
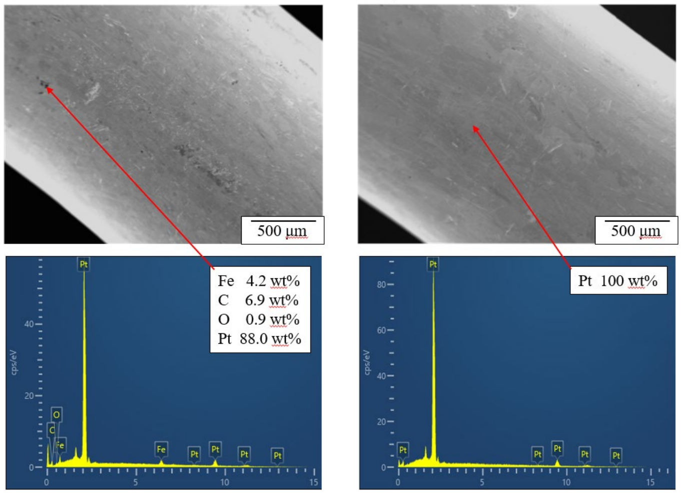


Fig. 1. Manufacturing process flowcharts for Conventional-Pt and Improved-Pt slugs.

RESULTS AND DISCUSSION

Figure 2 shows the SEM images and EDS analysis results of the surfaces of the Pt slugs. Clear black spots are distributed on the surface of the Conventional-Pt slug; however, no clear black spots are observed on the surface of the Improved-Pt slug. The EDS spectrum of a black spot on the Conventional-Pt slug contains obvious carbon-related peaks, indicating that the black spots on the surface are carbon precipitates. In addition to the C peak, Fe- and O-related peaks are detected on the surface of the Conventional-Pt slug. Because no other notable material-related peaks are observed, Fe is possibly present in an oxidized state. The Fe contaminant was probably trapped during the rolling/swaging process because the relatively hard Pt causes wear of the SUS rolling roller/drawing die via rubbing. Conversely, the Improved-Pt slug exhibits no evident C-, Fe-, or O-related peaks, owing to the new impurity-removal process.



(a) Conventional-Pt (b) Improved-Pt

Fig. 2. SEM images and EDS spectra acquired at the surfaces of Conventional-Pt (a) and Improved-Pt slugs (b). EDS analyses were performed at the points indicated by the arrows.

The average oxygen content in the Pt slugs, as measured by instrumental gas analysis, are presented in Figure 3. These are the average values from three samples of each Pt slug. The oxygen content in the Improved-Pt slug is reduced to approximately one-fifth of that of the Conventional-Pt slug. The drastic reduction in the O concentration can also be attributed to the newly proposed impurity-removal process.

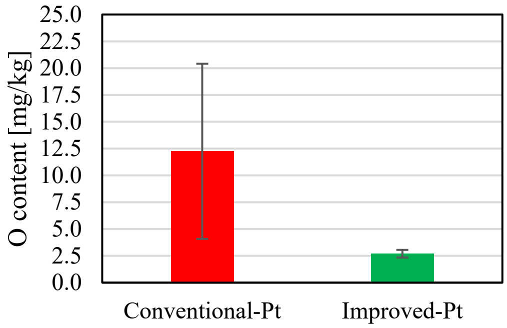
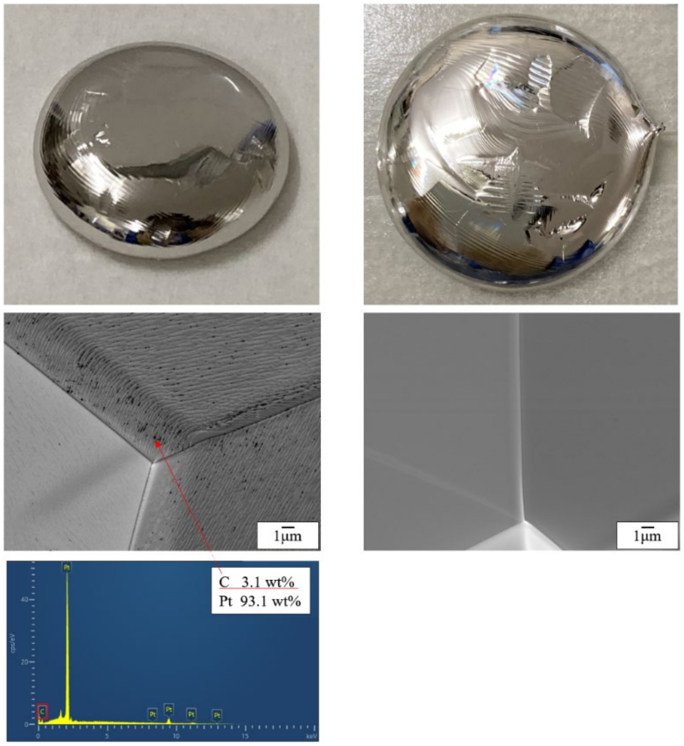


Fig. 3. Comparison of the average oxygen contents in the Conventional-Pt and Improved-Pt slugs.

Figure 4 shows the stereomicroscope and SEM images of the surface of the Conventional-Pt and Improved-Pt slugs removed from the hearth liner in the vacuum chamber of the EB evaporation system, after EB evaporation. No difference is observed between the stereomicroscopic images of the Conventional-Pt and Improved-Pt slugs. In previous investigations on the carbon-removal process and its applications to Au slugs [2], carbon contaminants in the Au slugs floated to the surface of molten Au and adhered as large visible black spots on the surface of the Au source after EB evaporation. Using the same analogy, it can be interpreted that carbon particles embedded within the conventional Pt slugs are released to float to the surface of molten Pt when the slugs are melted and formed into molten Pt by high-energy electron beams from an electron gun. However, the surface of the Conventional-Pt source after EB evaporation contains less floating carbon than Au, as can be observed from the stereomicroscopic images. This can be interpreted to be because of carbon and Pt forming a solid solution, making it difficult for them to float to the surface. Although SEM results reveal that small black spots of carbon precipitates are present on the surfaces of the melted Conventional-Pt slugs, the surfaces of the melted Improved-Pt slugs contain no black carbon residues. This difference indicates that the proposed impurity-removal and degassing processes are effective in reducing carbon contaminants in Pt slugs.



(a) Conventional-Pt (b) Improved-Pt

Figure 4. Stereomicroscope images, SEM images, and EDS spectrum acquired at the surface of Conventional-Pt (a) and Improved-Pt (b) after EB evaporation. EDS analysis was carried out at the points indicated by the arrows.

Figure 5 shows a particle map of the Pt-thin-film–deposited wafers evaluated using a defect/particle-inspection system. The defect/particle-inspection system can count particles with sizes ranging between 1 and 400 μm^2. The number of Pt nodules drastically decreased when Improved-Pt is used as the source material. The total number of particles on the Improved-Pt–deposited wafer is reduced to approximately one-seventh of that on the Conventional-Pt–deposited wafer. This improvement in nodule generation by Pt spitting is attributed to the reduction in contamination by the proposed treatment processes. In addition, considering the phase diagrams of Fe and Fe_xO_y, the trapped Fe_xO_y in the Pt slugs is reduced to Fe under high-temperature EB irradiation and vacuum conditions during evaporation. Therefore, oxygen outgassing owing to the reduction of Fe_xO_y may be related to Pt spitting.

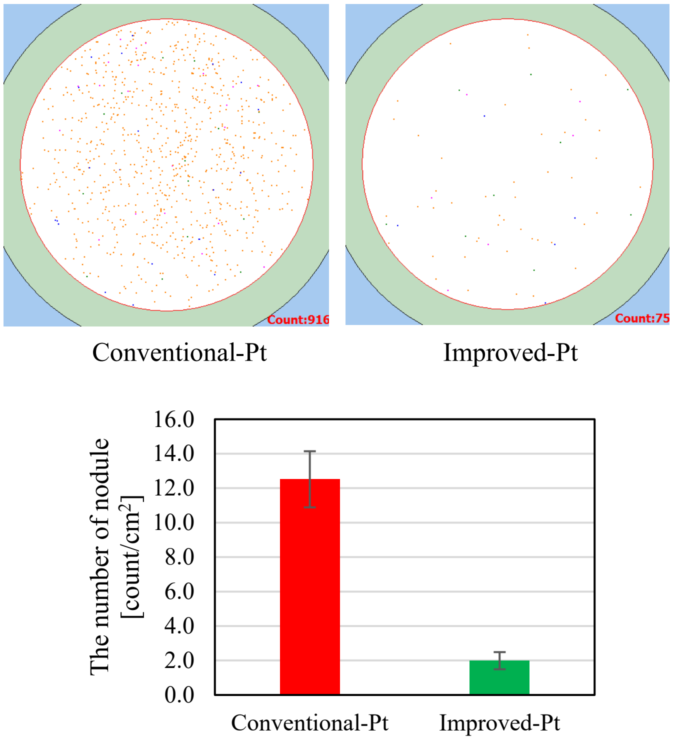


Fig. 5. Particle maps and number of nodules of Pt-deposited wafers.

Finally, we evaluated the specific electrical resistivity of the Pt films deposited with Conventional-Pt and Improved-Pt slugs. The specific electrical resistivity was measured at 17 points on the wafer. Figure 6 shows the average specific electrical resistances of the three Pt-deposited wafers. The Improved-Pt-deposited thin films had a lower specific electrical resistivity than the Conventional-Pt-deposited films. Although we did not investigate the quantitative relationships between each impurity concentration and specific electrical resistivity, in this study, the use of lower-impurity-contaminated slugs could possibly reduce the specific electrical resistivity of Pt-deposited thin films because the impurity concentration of Pt generally affects the specific electrical resistivity.

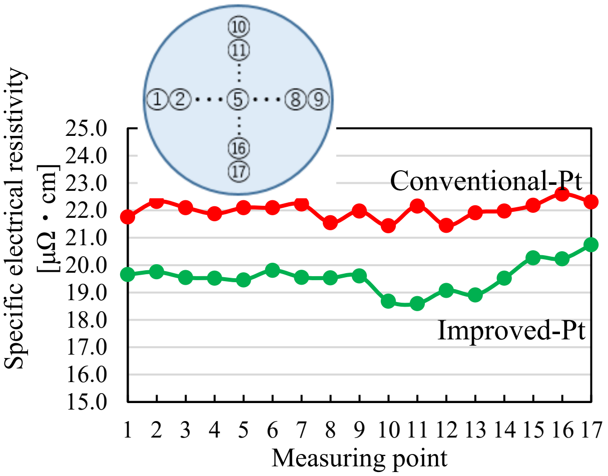


Fig. 6. Specific electrical resistivity of Pt thin films deposited with Conventional-Pt and Improved-Pt slugs.

CONCLUSIONS

We proposed a new impurity-removal process for the rolling and swaging steps and a new degassing process after the cutting process to reduce the entrapped contaminants in Pt slugs. To prove the effectiveness of the proposed processes, we evaluated the relationship between the Pt slug contamination and Pt-nodule generation by spitting during evaporation. The Pt slugs produced with and without the new impurity-removal and degassing processes were compared via surface SEM observations and EDS analyses, which revealed that the surface adhesion and embedding of carbon- and iron-related contaminants near the surface of the slugs were drastically reduced by the introduction of the proposed processes.

Consequently, the average number of particles on the Pt thin film deposited after the application of the new process (i.e., Improved-Pt) slugs was substantially reduced to approximately one-seventh of that of the conventionally processed (Conventional-Pt) slugs. In addition, the results of the specific electrical resistivity measurements indicated that the Pt thin film deposited with the Improved-Pt slugs had a lower specific electrical resistivity than that deposited with Conventional-Pt slugs. These results show that our proposed contamination-removal processes are very effective not only in manufacturing Pt slugs used as EB evaporation sources to improve Pt spitting but also in the formation of low-resistivity Pt thin films for compound-semiconductor devices.

ACKNOWLEDGEMENTS

The authors would like to thank the scientists and engineers at Ferrotec (USA) Corporation’s Temescal Division for their support, communication, and helpful discussions over the past five years.

REFERENCES

[1] K. Cheng, *Electron Radiation as an Indicator of Gold Nodule Defect during E-beam Evaporation*, 2011 CS Mantech Conference.

[2] T. Ito *et al*., *Gold-Assisted Deposition of a Material with Low Spitting by a New Carbon Removal Process*, 2023 CS Mantech Conference.

ACRONYMS

EB: Electron Beam

MNS: Matsuda New evaporation materials for Spitting reduction

FE-SEM: Field-Emission Scanning Electron Microscopy

EDS: Energy-Dispersive X-Ray