Standard Technical Procedure for Oxidation of Copper in a Resistive Furnace: An Approach for a Research Laboratory

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Abstract: ***Standardization through documentation of the thermal oxidation of copper in a muffle furnace is reported in this work. The standard was proposed by considering four sequential stages: development, evaluation, implementation and validation. Development involved technical analysis for proposing a documentation of the technical procedure. Evaluation stage was performed by revision and correction to the draft of the technical procedure by five reviewers. Implementation of the thermal oxidation of copper following the documented technical procedure was performed for two different users. The last stage (validation) involved comparison of the properties of two copper oxide sheets obtained by different users. In this stage, XRD patterns were used as an indirect measurement of reproducibility by comparing the number of peaks, intensity of the peaks, crystalline phases present in the copper oxide layer, and FWHM of the peaks. Additionally, weight and thickness measurements were included to the characterization of copper oxide. We have concluded that standardization of the technical procedure for thermal oxidation of copper in a research laboratory allowed to improve reproducibility in the properties of copper oxide.***

Keywords: Standardization; copper oxide; muffle furnace; research laboratory

1. Introduction

Standardization is a tool used for continuous improvement in an organization or industry. There are several benefits of the standardized work such as reduction of variability, reductions in injuries, easier training of new operators, among others [1]. There are three types of documentary standards from the viewpoint of the scope of the standard: formal, informal and private. In the field of formal standards, ISO (International Organization for Standardization) standards are a world reference in standardization of processes in industry and commerce [2-5]. There are some other areas where standards are frequently employed. For example, national governments develop documented regulations for managing their tasks [6]. On the other hand, although reproducibility is a key point in scientific research, the lack of standardized work has led to poor reproducibility [7, 8]. In fact, nowadays there is a reproducibility crisis in all research areas [9]. If continuous efforts to establish norms and standards are focused in scientific research, validity and reliability of research results can be considerably improved, which can have an impact in consistency and reproducibility of the results [10]. For example, copper oxide is a semiconductor with several applications in electronics and water purification [11, 12]. Thus, standardization of the copper oxide processes performed in universities or research centers can increase validity of the results on such topics. In the present work, the thermal oxidation of copper performed in a research laboratory was standardized through development of a technical procedure manual.

2. Materials and methods

Standardization of the process of thermal oxidation of copper using a muffle furnace involved four stages: development of the standard, evaluation of the standard, implementation of the standard, and validation of the results (figure 1). Oxidation of copper was performed in a resistive home-made muffle furnace. It has two main components of control and monitoring: a temperature controller (REX C-100) and temperature sensor (k-type thermocouple). Electrolytic commercial sheets of copper (99.9 % of purity) were used as raw material for thermal oxidation. For the development of the standard, the first step was to evaluate the potential for standardization of the thermal oxidation of copper process. Authors followed the decision tree proposed by Hatto [13]. After that, the following key points were also discussed:

- Aim to standard oxidation of copper in a muffle furnace.
- Scope of the proposal.
- Procedure for development of the draft.
- Selecting potential evaluators for the draft.
- Validation of the results.

In the design and elaboration of the standard, four main stages were identified: preparation of the copper sheets, characterization of the muffle furnace, oxidation of copper, and characterization of the copper oxide. Table 1 shows stages, steps, parameters to be controlled in each stage, and goals of the corresponding stage. The draft was then written as a technical procedure manual for oxidation of copper, and

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was divided in three main sections: preparation of the copper sheets, oxidation of copper, and characterization of copper oxide. In contrast with a simple instructive operation manual ("how to do it" section), the draft included a section where each step of the "how to do it" section was justified ("why do it"). In evaluation of a draft, Hatto indicates the sequential steps followed by ISO for publishing international standards [13]. The process initially begins making a proposal by a member of ISO, which delivers a draft and then is evaluated and corrected by members of a technical committee. The corrected draft is then delivered to the members of ISO. Approval of the standard is achieved if votes of at least 2/3 of "participant members" of the committee responsible for the document are in favour and no more than 1/4 of total votes are against. The final steps involve administrative procedures, which is out of the scope of this report. Once finished the draft, it was evaluated and improved by five researchers whose areas of expertise are close to the topic of the technical procedure reported in this work. Once evaluated and corrected, the standardized technical procedure manual was used to perform thermal oxidation of copper processes by different users. Parameters during oxidation of copper were: Temperature of oxidation (500 °C), time of oxidation (60 min), and atmosphere of oxidation (static air). The final stage of the oxidation of copper was characterization of the results. X-ray diffraction (XRD) measurements were performed with an X-ray diffractometer (XRD, Bruker D8 Advances) with a radiation of CuK□ (1.541 Å). Weight of the copper oxide samples was measured with an analytical balance model SF-400C. Thickness measurements were performed with a commercial micrometer (Digimatic Mitutoyo, H-2780). Results of characterization were compared and discussed to evaluate reproducibility of the results.

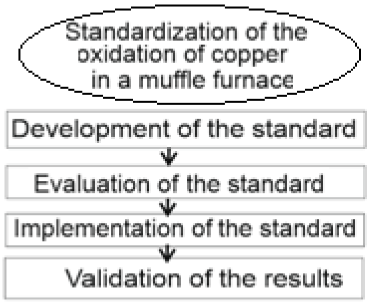

Figure 1: Scheme of the process followed for standardization of oxidation of copper in a muffle furnace

Table 1: Stages of the oxidation of copper in a muffle furnace considered for the design and elaboration of the standard.

Stage	steps	parameters to be controlled	Goal
Preparation of the copper sheets	• Sizing the copper sheets • Degrease of the copper sheets • Remotion of the native oxide from the surface of the copper sheets	• Volume of solvents • Volume of the Hydrofluoric acid (HF) • Time of agitation electrical power for agitation • Storage conditions of copper sheets after preparation	• Copper sheets free of grease, dust, and native oxide
Characterization of the muffle furnace	• Documentation of the controller parameters • Characterization of slope of heating and cooling	• Temperature vs time behavior • PID parameters	• Establishing a kind of thermal treatment • Avoiding to use different controller parameters
Oxidation of copper	• Heating copper in a muffle furnace	• Temperature • Time	• Growth of a copper oxide layer
Characterization of copper oxide	• Mass measurements • Thickness measurements • X-ray diffraction measurements	• Calibration of the micrometer • Calibration of the analytical balance • Parameters of measurement in X-ray diffraction equipment	• Reproducibility in structural properties of copper oxide

3. Results and Discussion

3.1 Development of the standard

As mentioned above, the standardized technical procedure document elaborated for thermal oxidation of copper included two general sections: "How to do it" and "why do it?. "How to do it" section contains detailed instructions for performing sequentially the tasks of the process for thermal oxidation of copper. Users of the manual are mainly undergraduate students or masters students. ¿Why do it? section was focused on justifying each one of the tasks performed in the "how to do it" section. This section can introduce new users in semiconductor process fabrication. Additionally, further evaluation by some experienced users can improve the standardized technical procedure. Criteria and justification for standardization of the thermal oxidation of copper based in the decision tree proposed by Hatto are shown in table 2.

Table 2: Criteria of the "decision tree" for standardization of thermal oxidation of copper, and justification for each criterion.

Criteria	Justification
Is the output a new and repeatable technique or procedure for:- identification,- characterization,- manipulation,- preparation,- verification,- etc. or is it the modification of an existing technique or procedure to allow its use under previously untested conditions?	It is not a new technique. However, in research laboratories, lack of reproducibility makes viable standardization of experimental processes such as thermal oxidation of copper
Does the output depend on the use of specific patents or specific pieces of commercial equipment?	No, the output does not depend on the use of specific patents due oxidation can be performed in home-made muffle furnaces
Has the output been evaluated by different investigators using different samples, materials, etc.?	Yes, several researchers have evaluated the process and they have concluded that changes in raw materials and the procedure affects reproducibility of the

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	results
Has the output been evaluated to determine its repeatability (same user) and reproducibility (different users)?	Yes, in both cases results such as structural characterization change dramatically when the same or different users perform the process
Have relevant databases been checked to ensure there are no pre-existing standards covering the same thing?	Yes, scientific literature and ISO standards were revised previously to propose a standardization of the thermal copper oxidation.
Are those involved in the development of the output prepared to work on developing a standard?	Yes, participants exhibit technical knowledge about the experimental process and also in developing a technical procedure

Table 3 shows the key points discussed after valoration of the decision tree for standardization of thermal oxidation of copper. The aim of this stage was to delimitate and establish a working route to develop the technical procedure document.

Table 3: Key points and conclusions discussed after evaluation of the decision tree

Key point	*Conclusion*
Aim of standardize thermal oxidation of copper process in a research laboratory	Improve reproducibility in the structural properties of copper oxide formed by thermal oxidation
Scope of the proposal	Standardization of this work is limited to a research laboratory. Validation of the results were limited to characterization of the structural properties of copper oxide by XRD technique, thickness and weight
Procedure for development of the draft.	The manual was proposed to divided in two sections: 1) How to oxidize copper in a muffle furnace. 2) Why each step of oxidation of copper is performed.
Selection of potential evaluators for the draft of the technical procedure document	Five evaluators were chosen according to their expertise in the area of semiconductors, manufacturing of processes, and structural properties of materials
Validation of the results	The results were validated through comparison of properties of copper oxide using: XRD patterns, thickness and weight measurements

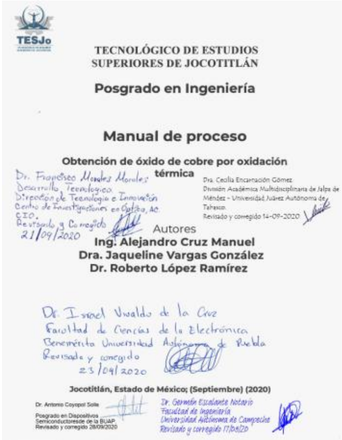
The last step of development of the standard was writing the draft of the technical procedure for thermal oxidation of copper.

3.2 Evaluation of the standard

Thermal oxidation performed to metals is a method commonly employed in the growth of semiconductors. This method exhibits some advantages such as:

- Simplicity of the process
- Low cost technique
- Non-dangerous
- Effective method for growth of semiconductor oxides

Evaluation of the draft of the technical procedure for thermal oxidation of copper was performed by five researchers whose area of expertise is closely related to oxidation of metals, manufacturing processes, and semiconductors. Once the draft was completed, it was sequentially sent to the five reviewers. After a period of revision and correction, the final draft was edited by the authors. Figure 2 shows the cover of the technical procedure document where the five researchers signed after approbation of the manual.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TECNOLÓGICO DE ESTUDIOS SUPERIORES DE JOCOTITLÁN

Posgrado en Ingeniería

Manual de proceso

Obtención de óxido de cobre por oxidación térmica

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Desarrollo Tecnologico
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Figure 2: Cover of the technical procedure document developed for standardization of the thermal oxidation of copper process. The signature of the five reviewers after revision and correcting of the draft is observed in the image.

3.3 Implementation of the standard

Figure 3 shows the muffle furnace and the copper sheets previous to a typical copper oxidation experiment in a muffle furnace.

Figure 3: Image of the muffle furnace and copper sheets used in the standardized process of thermal oxidation of copper

The two main parameters during thermal oxidation of copper were time of oxidation and temperature of oxidation. It is known that slope of heating or slope of cooling can directly affect structural properties of a material during thermal treatments. Thus, temperature vs time behaviour was characterized (figure 4). The Cu sheets were introduced into the furnace when the muffle was at room temperature. Thus, all processes were performed in identical conditions. The muffle furnace was then turned on and after 15 minutes (in

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which the temperature of the muffle was observed to be constant), the 60 min of heating was performed. The samples were cooled naturally and are extracted after 14 h when the muffle furnace reached room temperature. Implementation of the process of thermal oxidation of copper was performed by two different users which followed the detailed technical procedure for thermal oxidation of copper.

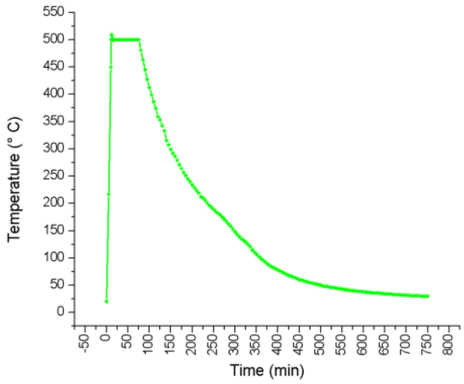

Figure 4: Temperature vs time graph characterized in a muffle furnace for standardized technical procedure of thermal oxidation of copper

3.4 Validation of the results

Reproducibility of the results was evaluated by comparing structural properties by XRD, weight and thickness of the samples. XRD is a technique that can be categorized as a fingerprint of the crystalline structure of a material. Figure 6 shows XRD patterns of two representative samples of copper oxide obtained by different users which followed the standardized technical procedure of thermal oxidation of copper. The samples were labeled as CuO-1 and CuO-2. In XRD pattern of CuO-1, there are five peaks which are placed at 2□= 29.44, 36.37, 42.15, 43.31, and 50.42 °. The peaks at 29.44, 36.37, and 42.15 ° correspond to (110), (111), and (200) planes of the cuprous oxide structure (PDF 00-005-0667). The intense peaks at 43.31 and 50.42 ° correspond to the (111) and (200) planes of metal copper (PDF 00-004-0836). XRD pattern of CuO-2 sample shows six peaks which are placed at 2□= 29.30, 36.21, 38.55, 42.04, 43.16, and 50.31 °. In Contrast to XRD pattern of CuO-1, only the peak at 2□=38.55 ° (which correspond to the (111) plane of the crystalline structure of cupric oxide (PDF 00-045-0937)) emerges in XRD pattern of CuO-2. The peaks of metal copper exhibit similar intensities, positions, and full width at half maximum (FWHM), which suggest that metal copper properties are similar in both samples. The cuprous oxide peaks are very similar in position and FWHM. However, intensity is stronger for CuO-2 peaks. Analysis of structural XRD patterns exhibits a mixture of copper, and copper oxide phases. From the view point of reproducibility, shift in position of the XRD peaks can be almost negligible due to internal stress at the structure of both copper oxide samples. Table 4 shows thickness and mass gain of CuO-1 and CuO-2. The thickness gain for both samples was in the range of 90-100 □m. The difference in thickness gain was 7 □m. The mass for both samples was in the range of 160-170 mg. The difference in mass gain was 6 mg.

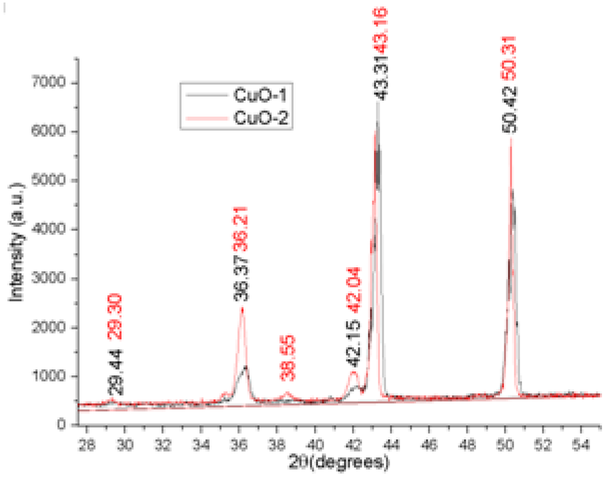

Figure 6: XRD patterns of two copper oxide samples performed by different users. Each user performed the experiment of oxidation of copper following instructions contained in the process manual reported in this work.

Table 4: Comparative of thickness and mass of two CuO samples obtained by different users which followed the standardized technical procedure of thermal oxidation of copper.

Sample	Copper thickness (µm)	Copper oxide thickness (µm)	thickness gain (µm)	Copper weight (mg)	Copper oxide weight (mg)	mass gain (mg)
CuO-1	209	300	91	70	168	98
CuO-2	213	311	98	70	162	92

4. Conclusions

Standardization of the technical procedure for thermal oxidation of copper using a muffle furnace was performed in this work. XRD, weight and thickness measurements showed that the properties of the copper oxide are similar if a standardized technical procedure is used, even when different users performed the experiment. Further changes to the standardized technical procedure manual can improve not only structural properties of copper oxide but also other properties such as electrical, optical, chemical and mechanical. This methodology can be used in research laboratories to improve reproducibility of results, which could be important in consistency of scientific research.

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