

# Vacuum oven to control the annealing process in alloyed nanolayers

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The design and construction of a vacuum quartz cylindrical oven to diffuse two or more metallic thin films for alloying is discussed. The oven has a gas-inert ambient (Ar) and a heater plate whose temperature is controlled by means of a home-made software development in LabView 7.0. The heater area of  $10 \times 5 \text{ cm}^2$  raises the temperature to  $600^\circ\text{C}$  over time due to the water-cooled extremes implemented. The oven is heated and controlled with a DC power supply, and a K-type thermocouple is used for monitoring the temperature with a  $\pm 0.1^\circ\text{C}$  resolution. Experiments done with the oven to obtain nanostructured AuCu alloys are detailed.

**Keywords:** Vacuum oven; metallic alloys; interdiffusion; controlled temperature.

En este trabajo se discute la fabricación de un horno al vacío basado en un tubo cilíndrico de cuarzo para difundir dos o más capas delgadas metálicas para formar una aleación. El horno trabaja en un ambiente inerte de argón (Ar) y una temperatura controlada a través de una plancha interior de cerámica y un sistema de control PID basado en un software desarrollado en LabView 7.0. El área de calentamiento de  $10 \times 5 \text{ cm}^2$  puede elevar la temperatura hasta  $600^\circ\text{C}$  debido a sus tapas circulares que cuentan con un sistema de enfriamiento de agua. El horno es calentado y controlado con una fuente de corriente directa y utiliza un termopar tipo K para monitorear la temperatura con una resolución de  $\pm 0.1^\circ\text{C}$ . Se detallan pruebas realizadas en el horno para obtener la aleaciones nanoestructuradas de AuCu.

**Descriptores:** Horno al vacío; aleaciones metálicas; interdifusión; control de temperatura.

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## 1. Introduction

Technological advances and scientific advances always go together, so electronic devices become an essential part of scientific experiments. The development of these devices involves a complex process, and a precise control of the different components' properties-morphology, crystalline structure and physical properties-is required. Therefore, scientists and technologists have created new experimental methods, tools and theoretical analysis to ensure that the materials developed are reliable. Thin film metallic alloys are a recent challenge in improving and extending the quality of the interconnecting electronic devices and their properties [1]. Cu-based alloys are widely used as conductor material due to their high electrical conductivity [2]. In particular, metallic alloys assume considerable importance in industrial applications where pure metals are widely used. This choice is motivated by better resistance to corrosion and better mechanical properties suited to the conditions in which they are used [3]. Nanotechnology is a recent field of science where the new materials and their applications involve a small size and the use of small quantities of material. Traditional high temperature ovens, designed to melt metals and produce alloys, permit better control of, and improved characteristics in the new materials. The preparation and characterization of the physical and morphological properties of alloyed nanofilms is a new opportunity for developing the ultra large scale integration (ULSI) field. With time, the electronic industry demands smaller-sized devices, and consequently, new techniques and methodologies for preparing and characterizing the new materials. There are many kinds of ovens for different appli-

cations; however, they are commonly used to melt materials and to prepare alloys [4, 5]. For alloy formation, the oven requires a higher control of the parameters such as range of temperature, control of temperature, pressure, type of atmosphere, heating and cooling velocities, etc. In this work, the design of a vacuum oven used to prepare thin film alloys is discussed. The oven works with a clean, inert atmosphere and allows a controlled temperature to diffuse binary and ternary materials to prepare controlled alloys. The proposed oven is used to anneal thin layers of materials and form alloys in a controlled manner. A nanostructured AuCu alloy was obtained as an example.

## 2. Oven design

The proposed oven was initially designed to prepare metallic alloys as the specific requirement; however, its utility can be extended to other processes. The main body of the oven consists in a transparent quartz cylindrical tube (pure  $\text{SiO}_2$ )

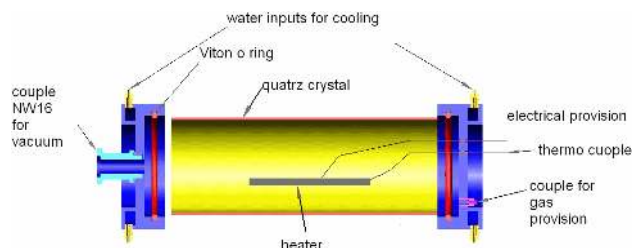


FIGURE 1. Vacuum oven for alloys preparation. Design and components.



FIGURE 2. Water cooled lids designed to seal the ends of the oven. Electrical feedthroughs and vacuum pump connection are shown.

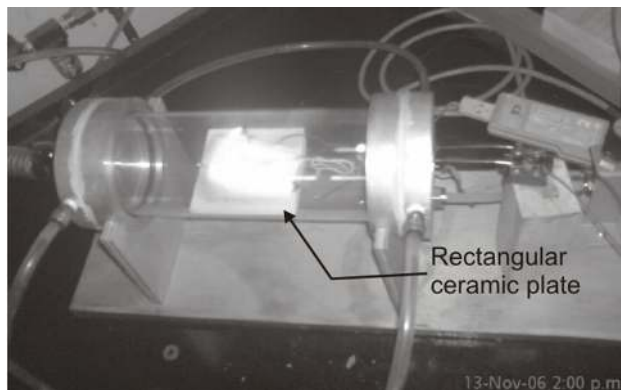


FIGURE 3. Home-made vacuum oven. The figure shows the rectangular ceramic plate when the samples are placed for heating.

with a wall 80 mm in diameter, 220 mm long, and 2 mm thick. The quartz tube open at both ends can withstand temperatures higher than 1500°C without strain and allows a clean atmosphere without contamination by the no-degasification during the heating process (Fig. 1). The thermal expansion coefficient is low ( $5.5 \times 10^{-7}^{\circ}\text{C}^{-1}$ ), and is almost impermeable to gases. The ends of the oven are sealed with aluminum lids which were designed with a double chamber where cooling water flows (Fig. 2). The ends are sealed with Viton O-rings to maintain the vacuum conditions when the inner air is removed with a vacuum pump. One aluminum lid of the oven contains NW16 vacuum connectors, a vacuum gauge connector and a valve to introduce air at atmospheric conditions. This side can be removed to introduce and take out the samples. The other lid contains the electrical connections, a thermocouple to measure the inner temperature and a connection for introducing inert gas. The samples to be annealed/diffused are placed on a ceramic plate ( $10 \times 5 \text{ cm}^2$ ), which is uniformly heated with a resistive wire (nichromel) with a DC power supply. The ceramic plate is placed in the center of the cylindrical oven also on a ceramic base (Fig. 3). The inner temperature is measured and controlled with a K-type thermocouple with an accuracy of  $\pm 0.1^{\circ}\text{C}$ . The desirable temperature is controlled with a

NI-DAQ card and home-made software developed in Lab-View 7.0.

### 3. Feedback control

An automatic controller is a hardware and software device that operates by monitoring the error signal, which is defined as the difference between the established value and the real value to be controlled. A proportional-integral-derivative (PID) controller is as effective in digital systems as it is in continuous systems. In fact, it is the most popular and commercially available controller used in the process industry [6]. A PID system is normally used to control a variable  $V_{in}$ , and can be represented by:

$$V_{in} = PE + I \int E dt + D \frac{dE}{dt} \quad (1)$$

In our case, the variable to be controlled is the oven temperature. The P, D and I constants are experimentally determined. In Eq. (1),  $V_{in}$  is the intake voltage applied to the system, and its value for time  $t$  depends on the error value  $E$  between the desirable value and the real value of the parameter to be controlled. In a discrete situation, when the error  $E$  is determined in every time interval  $\Delta t$ , the  $V_{in}$  value can be approximated by means of: [7]

$$V_{in} = PE + I\Delta t \sum_{m=0}^n E_m + \frac{D}{\Delta t} \{E_n - E_{n-1}\}, \quad (2)$$

where  $\sum E_m$  is the summation over all the error values determined since the control algorithm was turned on, and  $E_n$  is the  $n$ -th sampling.

All P, I and D parameters can be obtained by the Ziegler-Nichols method [6] and can be approximated by:

$$P = 0.6K_m \quad I = \frac{P\omega_m}{\pi} \quad D = \frac{P\pi}{4\omega_m} \quad (3)$$



FIGURE 4. Front panel designed in LabView for the control of the vacuum oven. The heating temperature in real time of the vacuum oven can be observed.

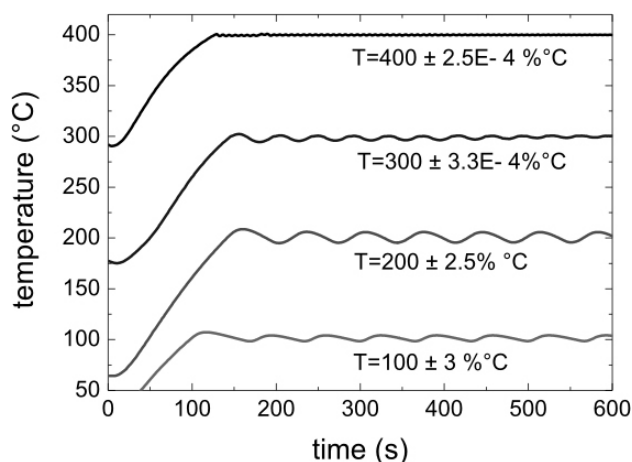


FIGURE 5. Heating curves for different controlled temperatures. The percentage of error for each temperature is shown.

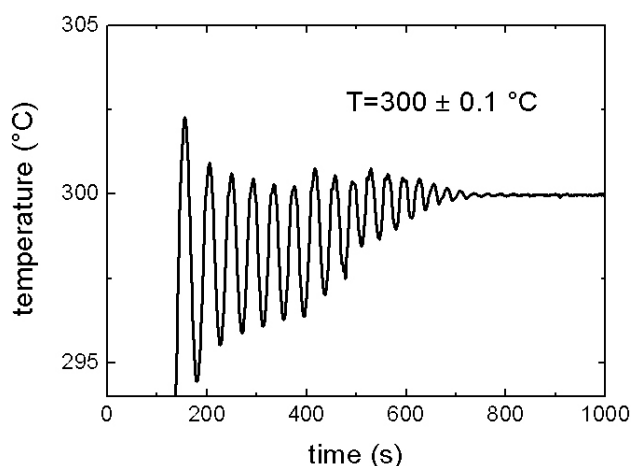


FIGURE 6. Detail of the heating process at 300°C. The error for this experiment is about  $\pm 0.1^\circ\text{C}$ .

The  $K_m$  constant is the gain at which the proportional part  $P$  (with values between 0 and 1) oscillates, and  $\omega_m$  is the oscillation frequency. The oscillation period  $T$  can be determined by running a closed loop step response with  $P = K_m$  and  $D = I = 0$ . When the system reaches the set-point temperature, the system oscillates around this temperature. The period of this oscillation needs to be known in order to adjust the PID parameters. The PID parameters can be redefined in terms of the period oscillation,  $T = 2\pi/\omega_m$ . Equations (3) can be re-written as:

$$P = 0.6K_m \quad I = \frac{PT}{8} \quad D = \frac{2P}{T}. \quad (4)$$

The parameters  $P$ ,  $I$  and  $D$  from Eq. (4) will be used to estimate the adequate PID parameters to obtain stability in the control of the oven temperature.

#### 4. Results

Initially, in order to obtain the values of the PID parameters, we proposed an arbitrary gain  $K_m$ . With this  $K_m$  value, the

mean oscillation period is measured and, consequently, the oscillation frequency. For our case, with the value  $K_m = 0.5$ , the PID parameters calculated from Eq. (4)  $P = 0.3$ ,  $I = 3.375$  and  $D = 0.0066$  gave stability and small error in the control system. This group of values was determined for our specific oven design, but these parameters can be quite different depending on the size, mass, temperature, and pressure of the oven to be controlled. Thus, a group of new PID parameters needs to be calculated for different ovens. Also, higher values of  $K_m$  gain cause higher errors in the first oscillation of the temperature. Then, a compromise between time response and difference in the error needs to be considered in order to obtain the PID parameters. Figure 4 shows a control panel designed in LabView 7.0 for our vacuum oven. From this panel, the following parameters can be controlled: on and off, desired temperature, experimental data filename, and PID values. Moreover, it is possible to visualize the real temperature of the oven as a function of time, error value (differences of temperature) and power supply (voltage and electrical current). Figure 5 shows typical heating curves for different controlled temperatures (100, 200, 300 and 400°C). Each curve shows the error percent obtained for each temperature. In the same figure it can be observed that the error diminishes when

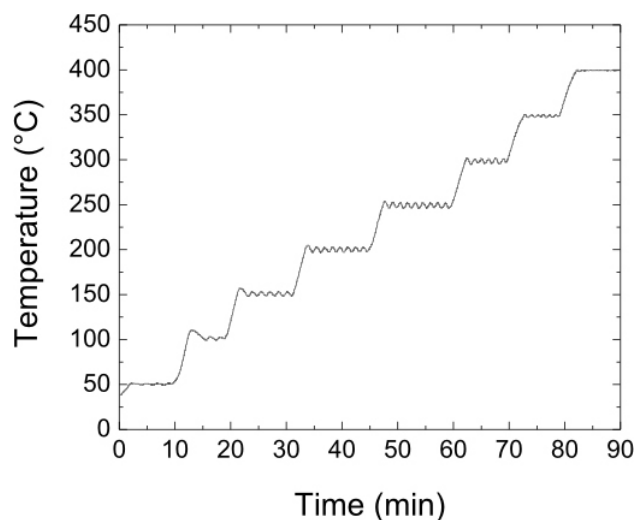


FIGURE 7. Steps heating curves obtained for different controlled temperatures in the vacuum oven.

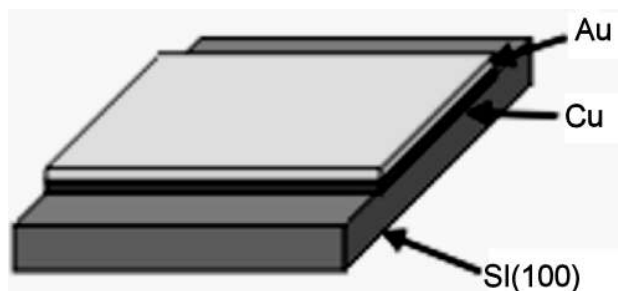


FIGURE 8. Au/Cu/Si system formed by thermal evaporation to form AuCu alloys in the implemented vacuum oven.

the temperature is controlled at 400°C as compared to 100°C; this means that the implemented system possesses more stability at high temperatures. This behavior could be due to the mass effect of the oven, with high temperatures and heavy masses being easier to control over time. Figure 6 shows a zoom for the heating curve controlled at 300°C. Here, it can be observed that the error decreases in time and tends toward a constant value ( $300 \pm 0.1^\circ\text{C}$ ) 10 min after the control was turned on (the heating process begins). Figure 7 shows the heating behavior, step by step when the oven was heated from 50 to 400°C in 50°C steps. From this, it can be seen that the control system reaches the desired temperature in 2 minutes approximately in each heating condition. As in Fig. 5, we concluded that the vacuum oven shows better stability at high temperatures. As an example of the application of the controlled vacuum oven, AuCu thin film alloys were prepared by diffusion. For this, Cu (99.999% purity) thin films ( $5 \times 20 \text{ mm}^2$  in size) were deposited on p-type Silicon (100) substrates 0.5 mm thick and  $10 \times 20 \text{ mm}^2$  in area by a thermal evaporation method in a vacuum chamber at  $10^{-5}$  Torr, evacuated with a turbomolecular pump. Au (99.999% purity) was subsequently deposited on the Cu films forming a bilayer (Fig. 8). The films deposited at a deposition rate of 0.5 nm/s were measured with a Maxtek TM-400 thickness monitor. The Au/Cu thickness ratio deposited corresponds to the atomic concentration of 50:50 (1:1.43) to form the AuCu alloy. After the bilayer deposition, the Au/Cu system was diffused by heating from room temperature (RT) to 300°C in the vacuum oven with Argon flow in order to avoid contamination and oxidation. Figure 9 shows zoom-sequential SEM images of the alloy formed after annealing from RT to 300°C in 1 hour. Crystals of AuCu alloy were formed as shown by the sequential images. Figure 10 shows the corresponding X-ray diffraction results for the Au/Cu bilayer and after diffusion for the alloy formation. The interdiffusion between Cu and Au to form the AuCu alloy was confirmed, where an intermetallic compound was formed instead the original bilayer before annealing. Figure 10 shows the main peak (111) of the AuCu alloy formed and its comparison with the Au/Cu bilayer before annealing [8]. Figure 11 shows the results of the corresponding EDS spectrum showing the atomic concentration analysis for the alloy formed. No oxygen content was detected due to the sealed, cleaned oven design. An atomic concentration ratio near 1:1 was measured, demonstrating the good reliability of the controlled oven for alloy preparation.

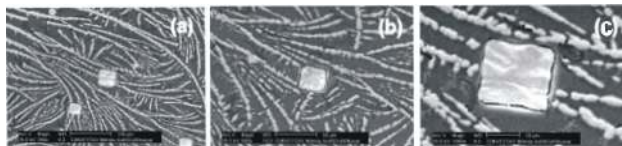


FIGURE 9. Sequential SEM images of AuCu/Si alloy (atomic concentration:1:1) after annealing at 300°C. Images show AuCu crystals. Lines of material correspond to the AuCu alloy. a) 250x, b) 500x and c) 1000x, magnifications.

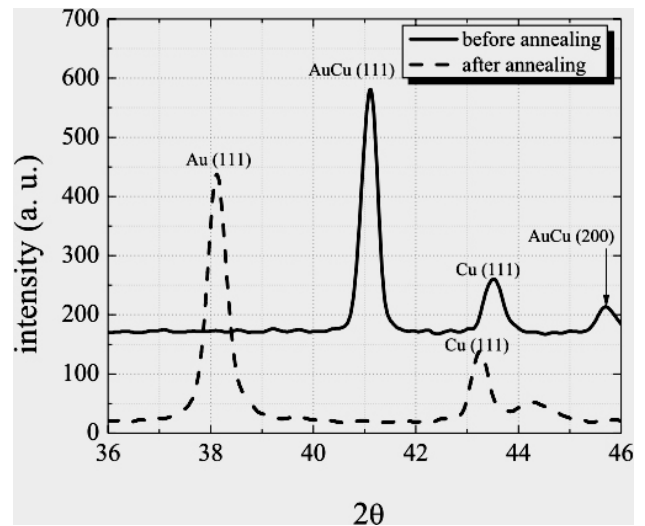


FIGURE 10. XRD spectra of Au/Cu/Si and AuCu before and after annealing (alloying) respectively. The atomic concentration for the sample was 1:1.

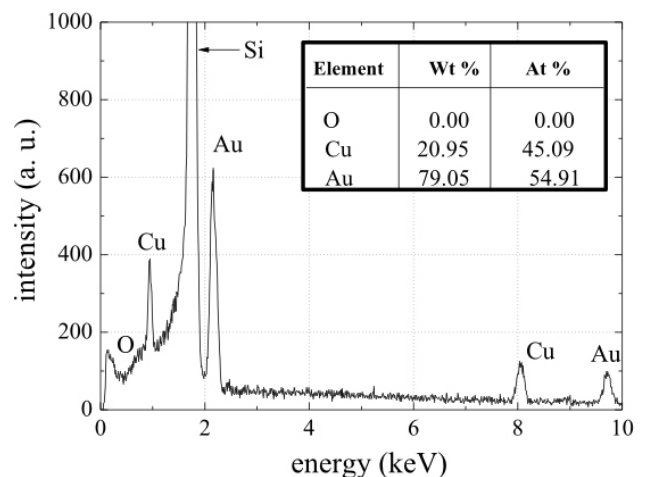


FIGURE 11. EDS analysis of the AuCu/Si after annealing. The measured atomic concentration was near 1:1.

## 5. Conclusions

The design of a vacuum oven to diffuse two or more metallic thin films to form thin film alloys with high stability temperature control was discussed. The vacuum oven is useful in studying the process of the alloy preparation in an inert atmosphere. The implemented system is controlled by a PC through home-made software developed in LabView 7.0. The group of PID parameters estimated presents better stability for higher temperatures (above 300°C). The stability of the implemented system was analyzed for different ranges of temperatures from 50 to 400°C. The controlled vacuum oven was used to prepare AuCu thin films alloys. Thin film bilayers were prepared on silicon substrate by thermal evaporation technique to form alloys. The AuCu alloy interdiffusion made into the vacuum oven from RT to 300°C were confirmed by EDS and DRX techniques. These results show

with success the interdiffusion for the AuCu bilayer formation.

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1. W. Zhang, S. H. Brongersma, O. Richard, B. Brijs, R. Palmans, L. Froyen, K. Maex. *J. Vac. Sci. Technol. B.*, **22**, (2004) 2715.
2. W. Pfeiler and B. Sprusil, *Mater. Sci. Eng. A*, **324**,(2002) 34.
3. J. Oudar, *Physics and Chemistry of Surfaces*, **Blackie & Son**, 1975, pp. 116 - 127.
4. D. A. Steigerwald and W. F. Egelhoff, Jr., *J. Vac. Sci. Technol. A*, **3123** (1989) 7
5. D. E. Nowak, B. Blank, A. Deyhim, and S. P. Baker, *AIP Conf. Proc.* **705**,(2004) 1146.
6. Bahram Shaian, Michael Hassul, "*Control System Design using MathLab*", Ed. Prentice Hall, ISBN 0-13-174061-X, (1993).
7. John Essick, *Advanced LabView Labs*, Ed. Prentice Hall, ISBN 0-13-833949-X, (1999).
8. R.D. Maldonado, A. I. Oliva, A.I. Oliva-Aviles, J. Perera-Borges, W. Cauich. J.E. Corona, O. Ceh. "*AuCu nanolayers: Deposition and characterization*". XVIII Latin American Symposium of Solid State Physics (SLAFES 06). Puebla, Puebla México. 20-24 November, (2006).