

Structural Properties of Spin Coated Multilayered Cupric Oxide Thin Films

P. Samarasekara, N. G. K. V. M. Premasiri*

Department of Physics, University of Peradeniya, Peradeniya, Sri Lanka

Abstract

CuO thin films were spin-coated at 1500, 2200 and 2400 rpm for 30 sec, and subsequently annealed at 150–550°C for 1 h. Multi-layered CuO thin films were prepared including three and five layers. These thin films were characterized using XRD, Fourier-Transform Infrared Spectroscopy (FTIR) and polarizing light microscopy. The XRD and FTIR analysis confirmed the crystallization of CuO phase in thin films annealed above 350°C, and corresponding crystallite sizes were observed to be increasing with the annealing temperature. The Scherrer formula was applied for (111) and $\bar{1}\bar{1}\bar{1}$ peaks of XRD patterns of CuO thin films. According to the data of $\bar{1}\bar{1}\bar{1}$ peak, average crystallite size increased from 0.801 to 55.2⁰Å as annealing temperature was increased from 350 to 500°C. In FTIR spectrum, peak corresponding to Cu-O bond appeared at wavelength of 532.4 cm⁻¹ above annealing temperature of 350°C.

Keywords: Spin coating, CuO, XRD, FTIR, Structure

*Author for Correspondence E-mail: pubudus@pdn.ac.lk

INTRODUCTION

Although both cupric oxide and cuprous oxide are copper based compounds, cupric oxide possesses much desired characteristics in a host of applications. Cupric Oxide is a predominant candidate in a host of applications including photovoltaics [1], nanoelectronics [2] and spintronics [3]. CuO is a black color compound with slight translucence.

This compound crystallizes in the monoclinic crystal system with lattice parameters: $a = 4.684 \text{ \AA}$, $b = 3.425 \text{ \AA}$, $c = 5.129 \text{ \AA}$ and $\beta = 99.28^\circ$ [1]. Furthermore, this material possesses some unique antiferromagnetic properties, and recent studies have revealed superconductive properties (high temperature superconductivity) as well [4].

In the context of photovoltaics, CuO is an interesting semiconductor of p-type having a direct energy band gap of 1.2–1.9eV [1]. These characteristics distinguish CuO as a promising candidate in manifold applications, especially pertinent to solar energy. Moreover, it is important as a selective solar absorber due to its high solar absorbance and low thermal emittance. When it comes to the realm of nanoelectronics, copper oxide is used

increasingly in a multitude of applications mingling with cutting edge technology. For instance, copper oxide is used in the form of a thin film to fabricate copper oxide hetero structures; these structures are proven to be applicable for large-area electrical devices.

CuO has been used in bilayer source-drain electrodes for Organic Thin Film Transistors (OTFTs) [2]. In addition, many different types of thin film transistors (TFT) are being experimented with this material. Cupric oxide has been proven to be a promising candidate in spintronics as well. CuO exhibits Room Temperature Ferromagnetism (RTF) [3], and thus this material offers a very good option for a class of spintronics, especially without the presence of any transition metal.

Besides the preceding major applications, cupric oxide has been found indispensable for diode fabrication [Au/CuO/p-Si metal/interlayer/semiconductor (MIS)] [5], battery preparation (as electrodes for lithium-ion micro-batteries) [6], catalysis [7], electrochemical cells [8] and so on.

Different types of preparation techniques have been successfully implemented for cupric oxide: sol-gel spin coating [1, 9], dc sputtering

[10], electrodeposition [11], spray pyrolysis technique [12], and so forth.

In addition, photovoltaic [10] and gas sensing [13] properties of sputtered copper oxide films have been investigated. The methane gas sensing properties of cuprous oxide synthesized by thermal oxidation was studied [14]. Low Cost p-Cu₂O/n-CuO Junction has been characterized [15].

In this report, structural properties of CuO thin films have been explained. Cupric acetate was used as the initial copper-containing material. In addition, two additives, namely ethylene glycol and polyethylene glycol were incorporated into the solution used for spin coating.

EXPERIMENTAL

Cupric acetate, diethanolamine and isopropyl alcohol were mixed together. The mole ratio between cupric acetate and diethanolamine was used to be 1:1. Then, a solution with Cu⁺² concentration of 1.5 mol dm⁻³ was prepared, using isopropyl alcohol as the solvent. Then, this solution was continuously stirred for 24 h. Thereafter, stirred solution was used for sol-gel spin coating.

Finally, spin coated thin films were annealed in air. In addition to the basic solution of Cu⁺², six different solutions were prepared using those two additives; three solutions per each additive, varying w/w %. For this purpose, the additives were included in the solution at the initial step of the experimental procedure. Three different spin rates (1500, 2200 and 2400 rpm), and two spin times (15 and 60 sec) were utilized to fabricate thin films.

On top of that, five different annealing temperature values with an increment of 100°C (150, 250, 350, 450 and 550°C), and two different annealing times (1 and 2 h) were used. Structural properties were determined using X-ray diffractometer (SIEMENS D5000). In addition to the JCPDS data card for CuO, "X Powder12" software (Martillo Sigmar Software, Spain) was used in the analysis. This software is rather accurate and convenient, especially in being calculated Full Width at Half Maxima (FWHM:β) corresponding to

different diffraction peaks. Fourier-Transform Infrared Spectroscopy (FTIR) was determined using Shimadzu IRPrestige-21.

Initially, a background analysis was performed using a cleaned piece of glass, and then thin film sample was analyzed for FTIR peaks. Universal Trinocular Polarizing Microscope (Euromex Universal Polarizing Microscope ME.2895) was employed to obtain the images of thin films.

RESULTS AND DISCUSSION

Two different ratios between cupric acetate and diethanolamine were experimented (1:1 and 1:2). Furthermore, three different concentrations for Cu⁺² were experimented (1, 1.5 and 2 mol dm⁻³). When Cu⁺² concentration was 1 mol dm⁻³, and the molar ratio was 1:2 (favoring DEA), thin film appeared to be patchy without having uniform distribution throughout the substrate, and this was observed in both as-prepared and after-annealed films prepared under those conditions (Figure 1a).

Moreover, when Cu⁺² concentration was adjusted to be 2 mol dm⁻³, film became uniform (Figure 1b). Consequently, it was found that 1:1 and 1.5 mol dm⁻³ makes the most appropriate combination for those two parameters. Although, three different spinning rates and two spin times were utilized, the appearance of the thin film did not show any differences at all.

Annealing time did not lead to any significant change in the appearance. But, annealing temperature was a very sensitive parameter in this aspect, because different annealing temperatures exhibited salient color changes in the thin films. Moreover, when it was attempted to anneal spin-coated thin films above 550°C, they tended to be unstable, especially due to the deformations of the substrate.

In addition to those bulk appearances, annealed thin films were observed under a magnification of (100×) in order to find whether those thin films are adequately uniform in this exaggerated view as shown in Figure 2.

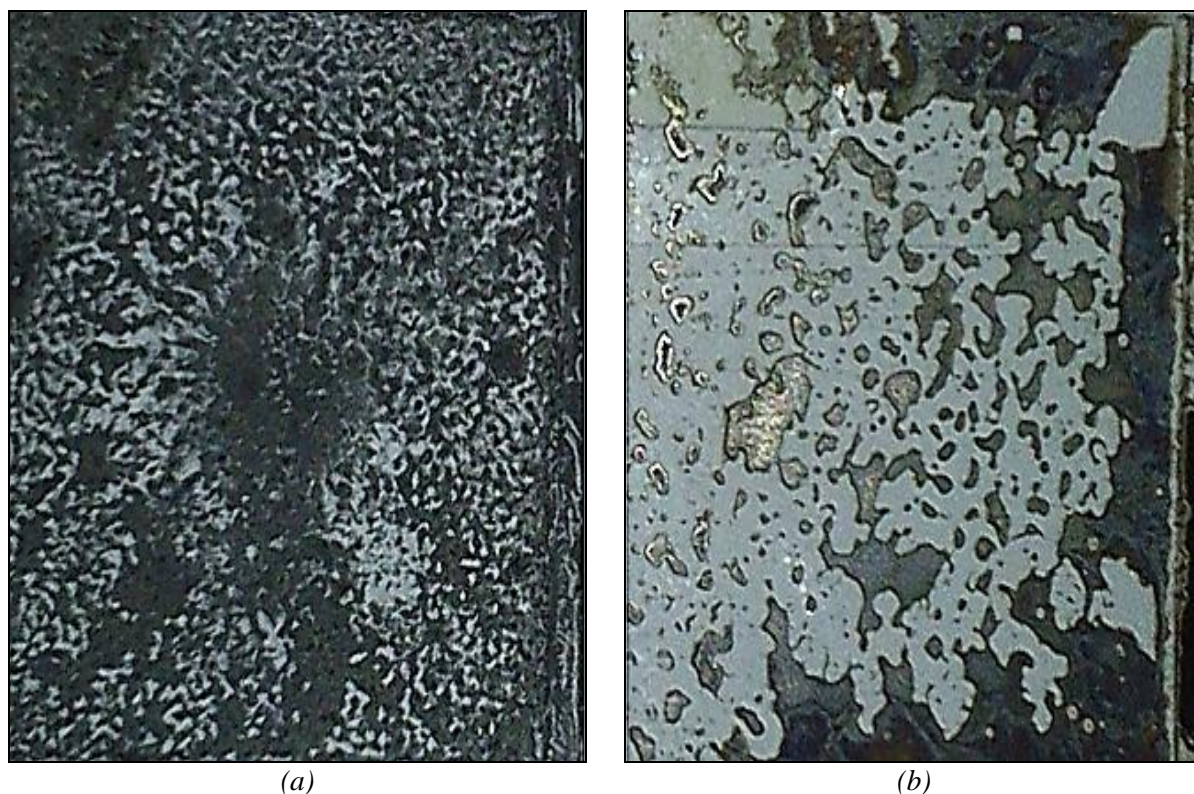


Fig. 1: (a) An Annealed Thin Film Prepared using a Solution of $[Cu^{+2}] = 1 \text{ mol dm}^{-3}$ and $Cu^{+2}: DEA = 1:2$, (b) an Annealed Thin Film prepared using a Solution of $[Cu^{+2}] = 2 \text{ mol dm}^{-3}$ and $Cu^{+2}: DEA = 1:2$.

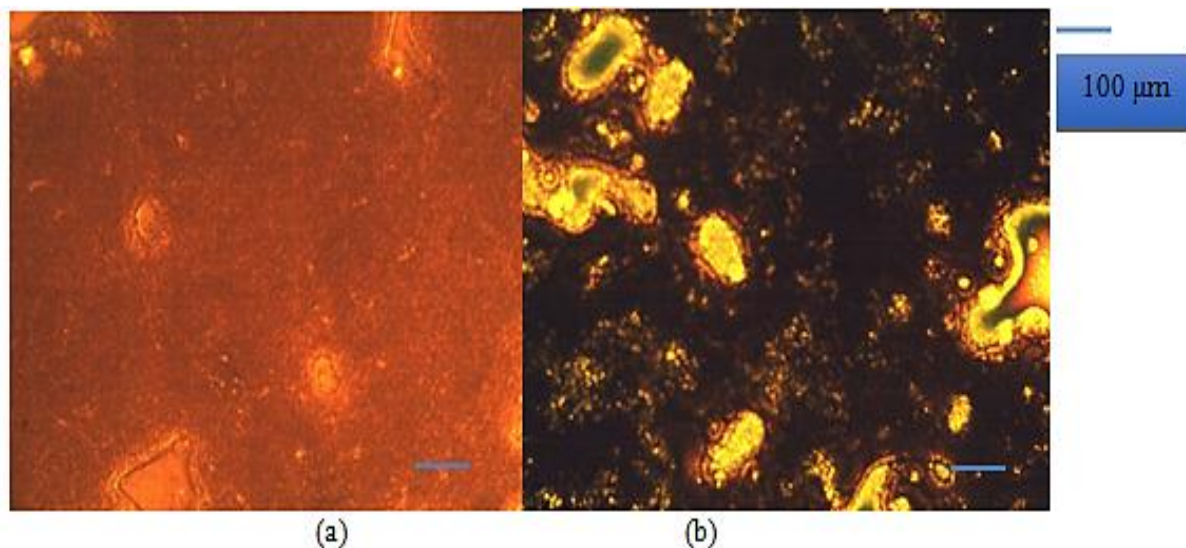


Fig. 2: Magnified Images of a Thin Film (annealed at 450°C) obtained for the (a) Reflection from the Film, (b) Transmission through the Film; using a Polarized Light Microscope.

Figure 3 shows the X ray diffraction patterns (XRD) of a CuO thin film annealed at different temperatures. There are basically two diffraction peaks identified to verify the formation of crystalline CuO, in comparison with the JCPDS (Joint Committee on Powder Diffraction Standards) data card for CuO

[Card No. 45-0937]. These two peaks indicate (111) and $(\bar{1}\bar{1}\bar{1})$ lattice planes of Cu corresponding to standard lattice spacing (d values) of 2.3120 and 2.5230 \AA , respectively. Corresponding experimental d values are 2.3141 and 2.5130 , respectively.

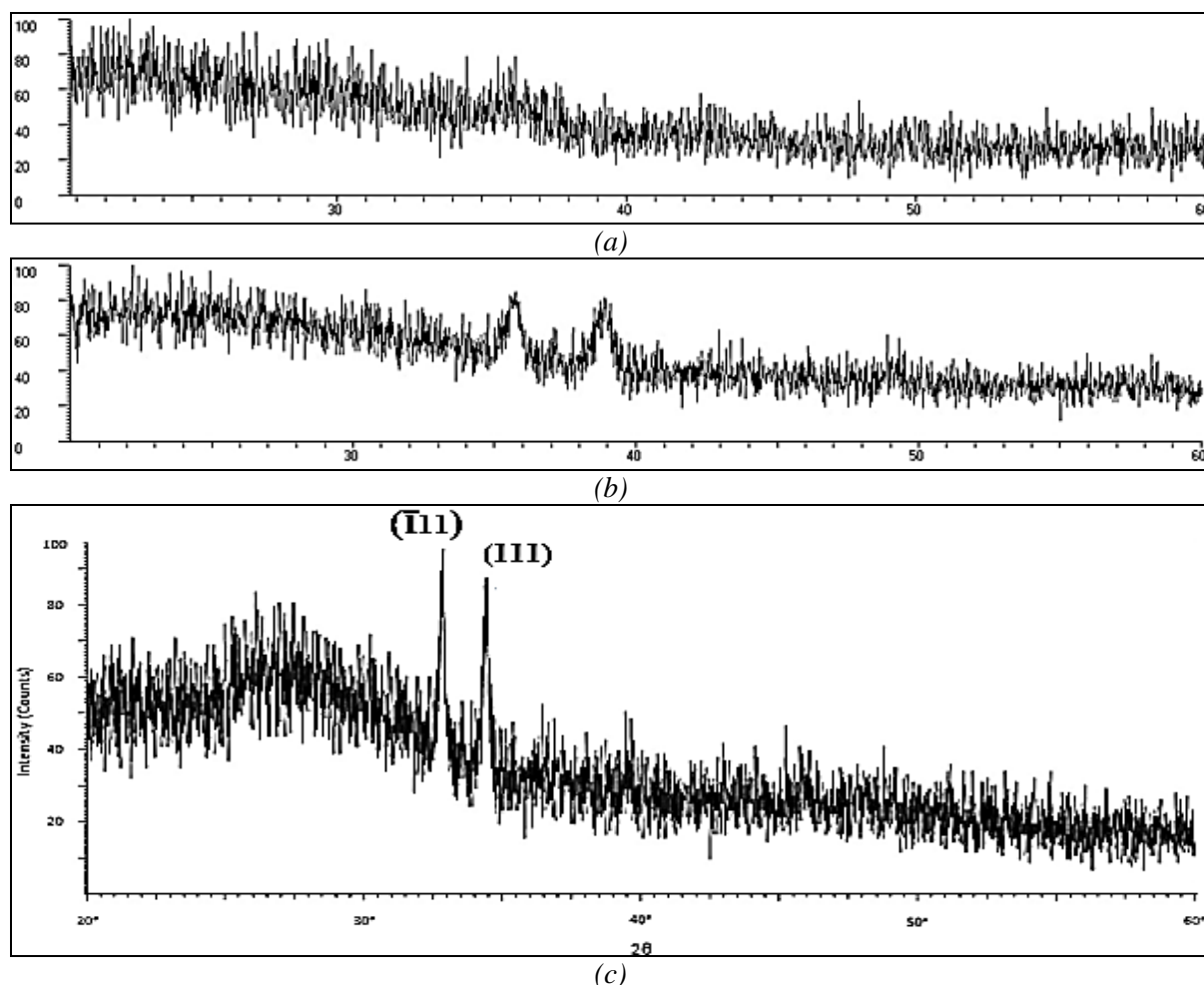


Fig. 3: XRD Pattern of a CuO Thin Film Annealed at (a) 150°C, (b) 350°C and (c) 550°C.

The Scherrer equation, $L = \frac{\kappa\lambda}{\beta \cos\theta}$, was applied to approximate the crystallite size of the CuO crystals formed in the thin films. Here L is crystallite size, κ is geometrical factor related to the shape of the crystallites (For a spherical shape crystallite, $\kappa \sim 1.07$, and CuO

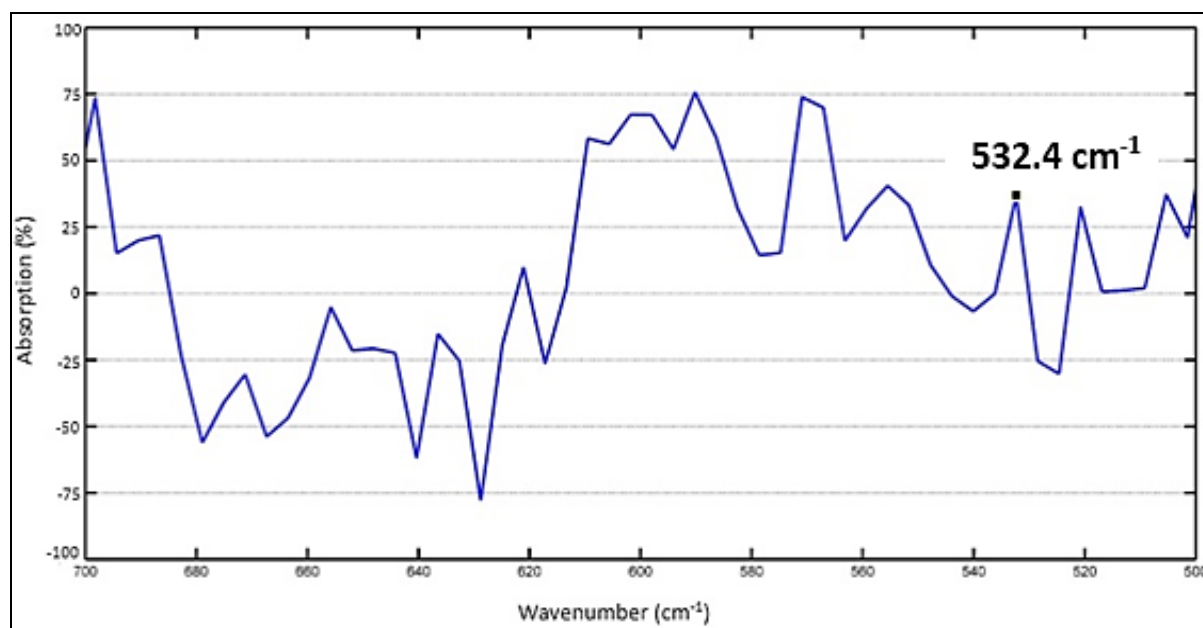
crystallites can be assumed to be approximately spherical), λ is wavelength of the used X-rays, β is full width at half maximum (FWHM) of the diffraction peak and θ is diffraction angle. Crystallite sizes of the CuO crystals formed in spin-coated thin films are tabulated in Table 1.

Table 1: Crystallite Sizes of Samples Annealed at Different Temperatures; Spin Rate = 2200 rpm; Spin Time = 60 sec; Annealing Time = 1 h, Calculated using $\kappa \sim 1.07$ and $\lambda = 1.5423 \text{ \AA}$.

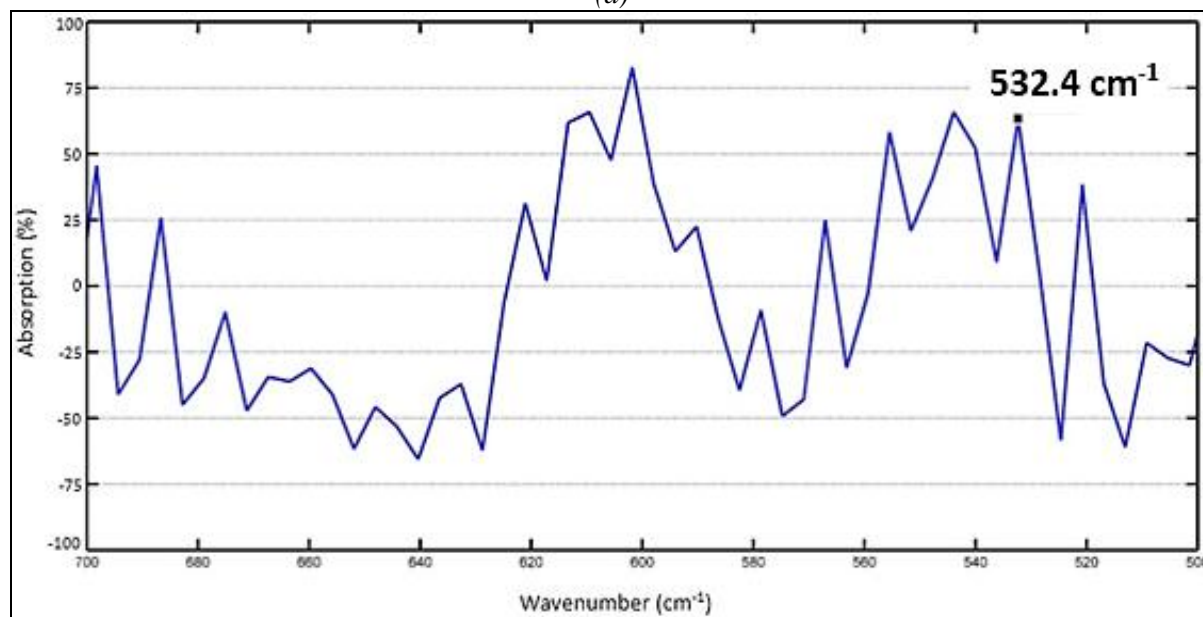
Annealing Temperature (°C)	Crystal Plane	θ (°)	β ($\times 10^{-2}$ rad)	L (Å)
350	($\bar{1}11$)	17.879	2.16	0.801
	(111)	19.411	2.06	0.850
450	($\bar{1}11$)	17.885	1.27	13.7
	(111)	19.408	1.21	14.5
550	($\bar{1}11$)	17.887	0.314	55.2
	(111)	19.402	0.349	50.1

Fourier-transform infrared spectroscopy along with XRD analysis was used to confirm the formation of Cupric Oxide in the thin films.

Thereupon, FTIR analyses were carried out for the thin films annealed at five different temperatures.



(a)



(b)

Fig. 4: The FTIR Spectrum of a CuO Thin Film Annealed at (a) 350 and (b) 550°C.

The FTIR spectra provide an explicit trend with respect to the characteristic Cu-O bond stretching corresponding to the wave number 532.4 cm^{-1} [1]. That is, as the annealing temperature is increased, the absorption percentage corresponding to the Cu-O bond stretching increases, implying the pronounced formation of cupric oxide at higher temperatures. Moreover, it was observed that for the temperatures of 150 and 250°C, Cu-O stretching does not exist at all, and the absorption begins to appear at 350°C, and eventually above 350°C this peak

substantiates, convincing the formation of cupric oxide (Figure 4).

CONCLUSION

XRD analysis verifies the formation of cupric oxide in the spin-coated thin films. Furthermore, the strong concordance between the d values (distances between parallel atomic planes) corresponding to the XRD analyses which were done in this research work and the experimental standards (Joint Committee on Powder Diffraction Standards) elaborates on this conclusion. In addition, the sequence of

XRD analyses in Figure 3 essentially conveys the appropriate annealing ambience required for a Cu(OH)₂ spin-coated thin film to convert that into (and crystallize) cupric oxide. This can be identified as annealing temperature of above 350°C, but it is evident that annealing temperature becomes rather desirable when it is in the region of 450–550°C, with increased intensities of diffraction peaks. Besides, approximating the crystallite size of the CuO crystals formed in the thin films using the Scherrer equation suggests that as the annealing temperature increases, corresponding crystallite size becomes larger. FTIR absorption peak of Cu-O bond appears only above the annealing temperature of 350°C implying that CuO phase can be crystallized only above 350°C.

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