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G.-R. Bai, A. Wang, C.M. Foster, and J. Vetrone

*Materials Science Division
Argonne National Laboratory
9700 S. Cass Avenue, Argonne, IL 60439*

*J. Patel and X. Wu
Physics Department
Northern Illinois University
DeKalb, IL 60115*

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Low-Temperature Growth and Orientational Control in RuO₂ Thin Films by Metal-Organic Chemical Vapor Deposition

G.-R. Bai, A. Wang, C. M. Foster and J. Vetrone
Materials Science Division,
Argonne National Laboratory,
9700 South Cass Avenue,
Argonne, IL 60439.

J. Patel and X. Wu
Physics Department
Northern Illinois University
DeKalb, IL 60115

ABSTRACT

For growth temperatures in the range of 275°C to 425°C, highly conductive RuO₂ thin films with either (110)- or (101)-textured orientations have been grown by metal-organic chemical vapor deposition (MOCVD) on both SiO₂/Si(001) and Pt/Ti/SiO₂/Si(001) substrates. Both the growth temperature and growth rate were used to control the type and degree of orientational texture of the RuO₂ films. In the upper part of this growth temperature range (~350°C) and at a low growth rate (<30Å/min.), the RuO₂ films favored a (110)-textured. In contrast, at the lower part of this growth temperature range (~300°C) and at a high growth rate (>30Å/min.), the RuO₂ films favored a (101)-textured. In contrast, a higher growth temperatures (>425°C) always produced randomly-oriented polycrystalline films. For either of these low-temperature growth processes, the films produced were crack-free, well-adhered to the substrates, and had smooth, specular surfaces. Atomic force microscopy showed that the films had a dense microstructure with an average grain size of 50-80 nm and a rms. surface roughness of ~3-10 nm. Four-probe electrical transport measurements showed that the films were highly conductive with resistivities of 34-40 μΩ-cm (@ 25°C).

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There has been considerable interest in the deposition of highly conductive metallic oxide thin films as metallization material for Very-Large-Scale-Integrated (VLSI) circuits. Ruthenium oxide, RuO_2 , has been studied due to its thermal stability, low resistivity, and superior diffusion barrier properties [1-5]. Various applications of RuO_2 thin films in integrated circuits have been explored [2,6]. For example, the use of RuO_2 thin films as precision resistors in integrated circuits (IC's) has been extensively investigated [7-9]. Recently, RuO_2 thin films have been studied as electrode layer for integrated ferroelectric or high- ϵ (dielectric constant) thin-film storage-node capacitors [10-16] in high-density dynamic-random-access (DRAM) and non-volatile (NVRAM) memory applications. By using RuO_2 thin-film electrodes as opposed to conventional Pt electrodes, the polarization fatigue resistance of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT)-based thin film capacitors can be dramatically improved [11,17,18], particularly for compositions near the morphotropic boundary [19].

A variety of thin film deposition techniques, including RF-magnetron [3,13,16] and DC-sputtering [2,7-9], RF reactive sputtering [4,5,12,14,15,17], pulsed laser deposition (PLD) [20], and metal-organic chemical vapor deposition (MOCVD) [1,21,22], have been used to fabricate RuO_2 thin films. Among these methods, MOCVD offers the significant advantages for the high-density IC fabrication: well-developed tool clustering and design, excellent composition and thickness uniformity, high deposition rates, superior step coverage and via infiltration capability, and scalability to large wafer sizes. However, in previous reports of the deposition RuO_2 thin films using MOCVD [1,21], the growth temperatures were high ($>550^\circ\text{C}$) resulting in films with a random polycrystalline structure. These films exhibited a high electrical resistivity ($60\text{-}90\ \mu\Omega\text{-cm}$ @ 25°C) when compared to that of bulk RuO_2 ($35.2 \pm 0.5\ \mu\Omega\text{-cm}$ @ 25°C [23]). $\text{Pb}(\text{Zr}_{0.82}\text{Ti}_{0.18})\text{O}_3$ thin films deposited on these RuO_2 electrodes showed inferior polarization hysteresis [24] as compared to PZT films grown on Pt electrodes [10-11,19], even after post-growth high-temperature annealing. Recently, lower-temperature MOCVD processing ($\sim 350^\circ\text{C}$) of RuO_2 thin films has been reported [22]. These films were randomly-oriented polycrystals on $\text{SiO}_2/\text{Si}(001)$ substrates and also showed higher-than-bulk resistivity ($60\ \mu\Omega\text{-cm}$ @ 25°C).

For many electronic or optical device applications, RuO_2 thin films that are structurally highly-textured are more attractive than randomly-oriented polycrystalline films for three reasons. First, such films typically have a dense columnar-grained microstructure. Since grain boundary scattering is a dominant electron-scattering mechanism in RuO_2 [25], RuO_2 thin films with an ordered microstructure should show a lower resistivity. Second, a highly-textured RuO_2 layer can better serve as a structural template for subsequent growth of multi-layer structures, particularly for amorphous substrate surfaces such as $\text{SiO}_2/\text{Si}(001)$. Third, if the preferred orientation of the RuO_2 layer can be controlled, the orientation of subsequent layers can be controlled. In this letter, we present low-temperature growth processes for highly-textured RuO_2 thin films

on SiO₂/Si(001) and Pt(111)/Ti/SiO₂/Si(001) substrates using MOCVD. We describe the structure and electrical conductivity of the deposited RuO₂ films with an emphasis on the correlation of the growth parameters, particularly the growth temperature and growth rate, to the film structure.

The deposition of RuO₂ thin film was carried out in a low-pressure, horizontal, cold-wall, quartz reactor with a resistive substrate heater. Si(001) with a native SiO₂ layer and Pt(111)/Ti/SiO₂/Si(001) wafers were chosen as substrates. Prior to the RuO₂ deposition, the substrates were cleaned using a sequence of acetone, methyl alcohol, and de-ionized water. Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) ruthenium, Ru(TMHD)₃, was used as the ruthenium precursor. The organometallic precursor vapors were introduced into the reactor via a high purity nitrogen carrier gas. Film growth rate was controlled by adjusting the carrier gas flow and the ruthenium source temperature. Pure oxygen was used as the oxidant and introduced into the reactor through a separate line. The details of the reactor design and deposition procedures have been previously reported [26]. The optimized growth conditions for obtaining textured RuO₂ films on SiO₂/Si(001) and Pt(111)/Ti/SiO₂/Si(001) substrates are shown in Table 1.

TABLE 1. Growth Conditions for RuO₂ Thin Films

Substrate Temperature	250-600 °C
Reactor Pressure	4 torr
Ru(TMHD) ₃ Precursor Temperature	112-118 °C
Flow Rate of O ₂ Reactant Gas	120 sccm
Flow Rate of N ₂ Carrier Gas	20-50 sccm
Flow Rate of N ₂ Background Gas	50 sccm
Film Thickness	1000 -1500 Å
Film Growth Rate	20 -40 Å/min.
Substrate Materials	SiO ₂ /Si(001), Pt(111)/Ti/SiO ₂ /Si(001)

The dependence of structure and crystallinity of the deposited films on the growth parameters, such as growth temperatures and growth rates, were investigated using x-ray diffraction. Film thickness was measured from a Dektak 3030 surface profilometer. Surface roughness and morphology of RuO₂ films were analyzed using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Four-point probe measurements were used to characterize the conductivity of RuO₂ films.

First, while keeping all other growth conditions constant, we investigated the effect of growth temperature on RuO₂ thin films deposited on SiO₂/Si(001) substrates. For RuO₂ films grown above 500°C, the film surface appeared very rough, sometimes containing cracks, and occasionally peeling away from the substrate. The resistivity of these films was above 1000 μΩ-cm. For RuO₂ films grown below ~250°C, the films were smooth, amorphous and also highly resistive. For RuO₂ films grown between 250°C and 450°C, the films were smooth and highly conductive; however, the structure of the films was very sensitive to the growth temperature. When the growth temperature was higher than 425°C, the films were always polycrystalline with random orientation. However, as the growth temperature decreased, the structure of the films tended to texture. Furthermore, the texture of the RuO₂ films could be controlled depending on the growth temperature. In Fig. 1, we show the x-ray θ-2θ scans for RuO₂ films processed at three different growth temperatures in this range. The film grown at 425°C (upper) is polycrystalline with no preferred orientation. In contrast, the film grown at 350°C (middle) is highly (110)-textured and the film grown at 300°C (bottom) is highly (101)-textured.

Second, we also studied the effect of growth rate on the degree of structural texture of the deposited films. In Fig. 2, we show x-ray θ-2θ scans for RuO₂ films grown at two different growth rates at growth temperatures of 350°C (a) and 300°C (b). For RuO₂ films grown at 350°C (Fig. 2a), a growth rate of greater than 30 Å/min. reduced the degree of (110) texture (upper), as indicated by the appearance of RuO₂ (101), (200) and (211) peaks in the x-ray pattern. In contrast, a growth rate of less than 30 Å/min. resulted in a high degree of (110) texture (lower). For RuO₂ films grown at 300°C (Fig. 2b), a growth rate of less than 30 Å/min. reduced the degree of (101) texture (lower), as indicated by the appearance of RuO₂ (110), (200) and (211) peaks in the x-ray pattern. In contrast, a growth rate of greater than 30 Å/min. resulted in a high degree of (101) texture (upper).

Based on above observations, we draw the following conclusions. First, as the growth temperature decreases, the RuO₂ thin films on SiO₂/Si(001) tend to structurally texture. Second, for a fixed growth rate in this low-growth-temperature regime, increased growth temperature favors (110)-textured films; whereas, decreased growth temperature favors (101)-textured films. Third, for fixed growth temperature, lower growth rates favor (110)-textured films, and higher growth rates favor (101)-textured films.

The structural texturing of thin films on amorphous surfaces has been treated extensively [27]. In this case, since the native SiO₂ layer of the Si(001) surface is amorphous, it is expected that the film nucleation process on this surface should be isotropic, irrespective of growth temperature and growth rate. However, since the structure of RuO₂ is tetragonal, the growth of the nucleation centers once they are formed will be anisotropic, with film growth in specific crystallographic direction favored over others. When the growth temperature is high (i. e., >400°C

for RuO₂), adatoms have sufficient thermal energy to diffuse and migrate on the SiO₂/Si(001) surface so that the growth rate of nucleation crystallites of various orientation are relatively equivalent. Consequently, the resultant structure of the film is a randomly-oriented polycrystal.

In contrast, for low growth temperatures (i. e., <400°C for RuO₂), adatoms are less mobile which results in the suppression of crystallite growth in some direction. Consequently, the film become textured. We have previously reported similar low-temperature texturing in MOCVD-processed PbTiO₃ thin films grown on SiO₂/Si(001) [28]. Furthermore, changes in the arrival rate of reactants at substrate surface changes the degree of supersaturation of the vapor phase. This can also strongly affect the texturing of the film changing the nucleation density on the substrate surface. This either increases or decreases the required diffusion distance for adatoms to reach nucleation centers, and consequently affects the structural texture of the film [27]. These process have been previously discussed theoretically [29].

It has been shown that by using a composite electrode structures of RuO₂/Pt, PZT-based capacitors do not exhibit the high-leakage-current densities typical of RuO₂ electrodes neither the substantial cyclic fatigue associated with Pt electrodes [18]. Consequently, we have also studied the textured growth of RuO₂ films on Pt(111)/Ti/SiO₂/Si(001) substrates. As shown in Fig. 3, the growth-temperature (a) and growth-rate (b) dependence of the structural texture of RuO₂ films deposited on Pt(111)/Ti/SiO₂/Si(001) substrates is similar as that observed for SiO₂/Si(001) substrates. Fig. 3a shows the x-ray θ - 2θ scan results for RuO₂ films grown at 350°C (upper) and 300°C (lower), respectively. The structure of RuO₂ films grown at 350°C is (110) textured while that of films grown at 300°C is (101) textured. Fig. 3b shows the x-ray θ - 2θ scan results for RuO₂ films grown at 300°C on Pt(111)/Ti/SiO₂/Si(001) but at different growth rates. For a growth rate of less than 30Å/min. reduced the degree of (101) texture (lower), as indicated by the appearance of RuO₂ (110), (210) and (211) peaks in the x-ray pattern. While a growth rate of greater than 30Å/min. resulted in a high degree of (101) texture (upper).

All the RuO₂ films grown in the temperature range of 275-425°C are crack-free, uniform and specular morphology, adhering well to both SiO₂/Si(001) and Pt(111)/Ti/SiO₂/Si(001) substrates. In Fig. 4, we show AFM micrographs of the surface of 1500Å-thick RuO₂ films grown on SiO₂/Si(001) at 350°C with (110)-texture (a) and at 300°C with (101)-texture (b). From the images, we can see that both types of films had dense microstructures with an average grain size of 500-800Å. We determined that the films exhibited root mean squared roughness over an area of 25 μm^2 of 10.1 ± 0.2 nm for (110) textured films (a) and 3.5 ± 0.2 nm for (101) textured films (b). Using the four-point probe method, we found that all the RuO₂ films grown in the temperature range of 275-425°C had typical resistivities of 34-40 $\mu\Omega\text{-cm}$ @ 25°C. These resistivities are very close to that of bulk RuO₂ [23], lower than that reported previously for MOCVD-grown RuO₂ films [1,21,22], and similar to that reported for epitaxial RuO₂ film grown by PLD on

Si(001) using yttria-stabilized zirconia buffer layers [20]. We have also previously shown that MOCVD-processed $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ thin films deposited on the (110)-textured RuO_2 electrodes exhibited excellent ferroelectric hysteresis and fatigue characteristics [30].

In summary, at temperatures as low as 275°C, highly conductive RuO_2 thin films with either (110)- and (101)-textured orientations have been grown by MOCVD on both $\text{SiO}_2/\text{Si}(001)$ and $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}(001)$ substrates. The structural texture of the RuO_2 films was controlled by both growth temperature and growth rate. Higher growth temperatures and lower growth rates favor growth of (110)-textured films, while lower growth temperatures and faster growth rates favor growth of (101)-textured films. All the RuO_2 films grown in the temperature range of 275-425°C are crack-free, uniform and specular morphology, adhering well to both $\text{SiO}_2/\text{Si}(001)$ and $\text{Pt}(111)/\text{Ti}/\text{SiO}_2/\text{Si}(001)$ substrates with typical resistivities of 35-40 $\mu\Omega\text{-cm}$ @ 25°C.

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Figure Captions:

- Figure 1: X-ray diffraction patterns of RuO₂ films on SiO₂/Si(001) showing changes in the type and degree of structural texture for films processed at different growth temperatures: 425°C (upper), 350°C (middle) and 300°C (bottom).
- Figure 2: X-ray diffraction patterns of RuO₂ films on SiO₂/Si(001) showing the effects of growth rate on the degree of structural texture for films processed at two growth temperatures: (a) 350°C and (b) 300°C. The upper curves are for high growth rates (>30 Å/min.) and the lower curves are for low growth rates (<30 Å/min.).
- Figure 3: X-ray diffraction patterns of RuO₂ films on Pt(111)/Ti/SiO₂/Si(001) substrates showing the growth-temperature (a) and growth-rate (b) dependence of the structural texture. Shown two growth temperatures: 350°C (a, upper) and 300°C (a, lower) and two growth rates for films grown at 300°C: <30Å/min. (b, lower), and >30Å/min. (b, upper).
- Figure 4: AFM micrographs of the surface of 1500Å-thick RuO₂ films grown on SiO₂/Si(001) at 350°C with (110)-texture (a) and at 300°C with (101)-texture (b).

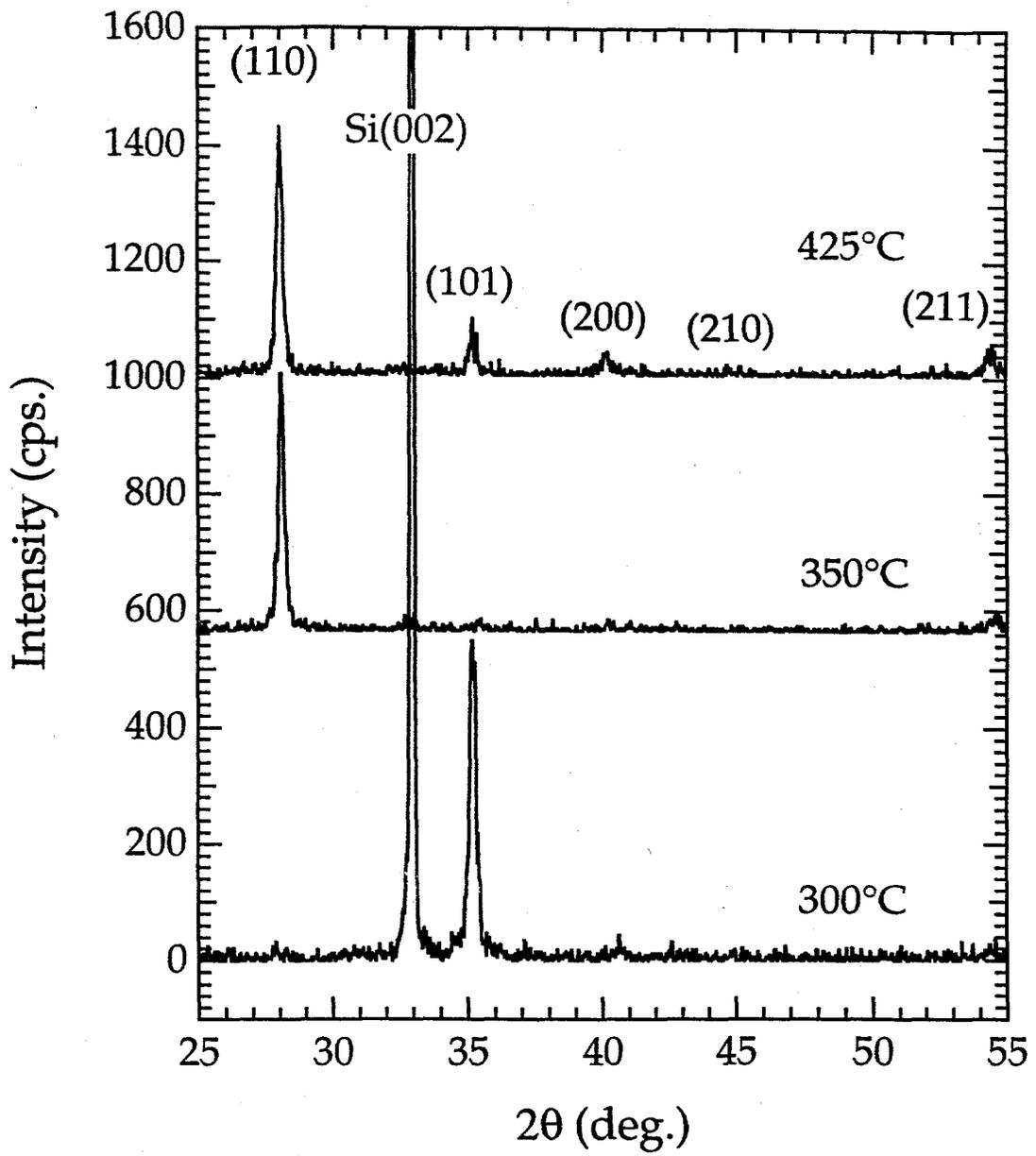


FIG. 1

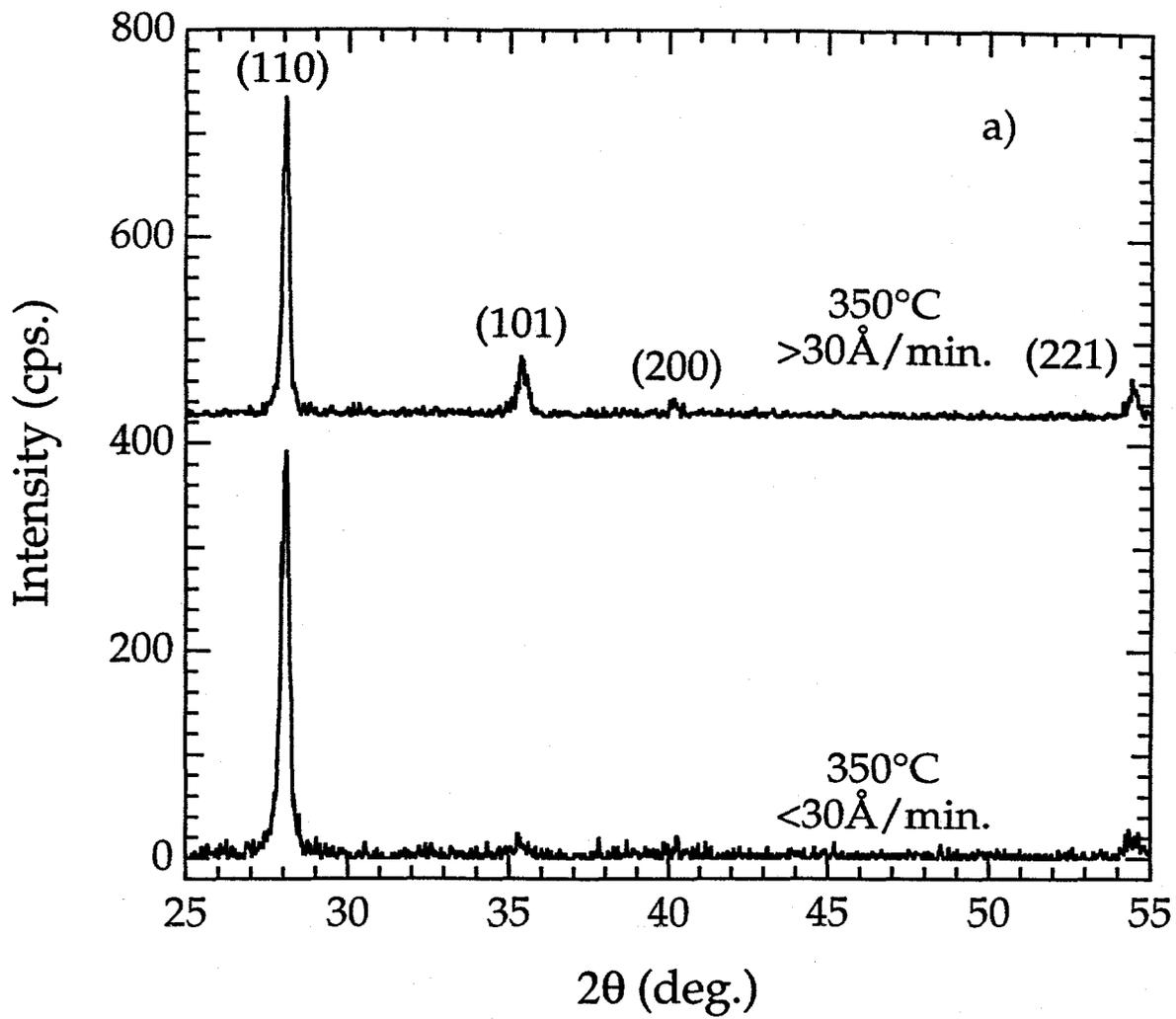


FIG. 2A

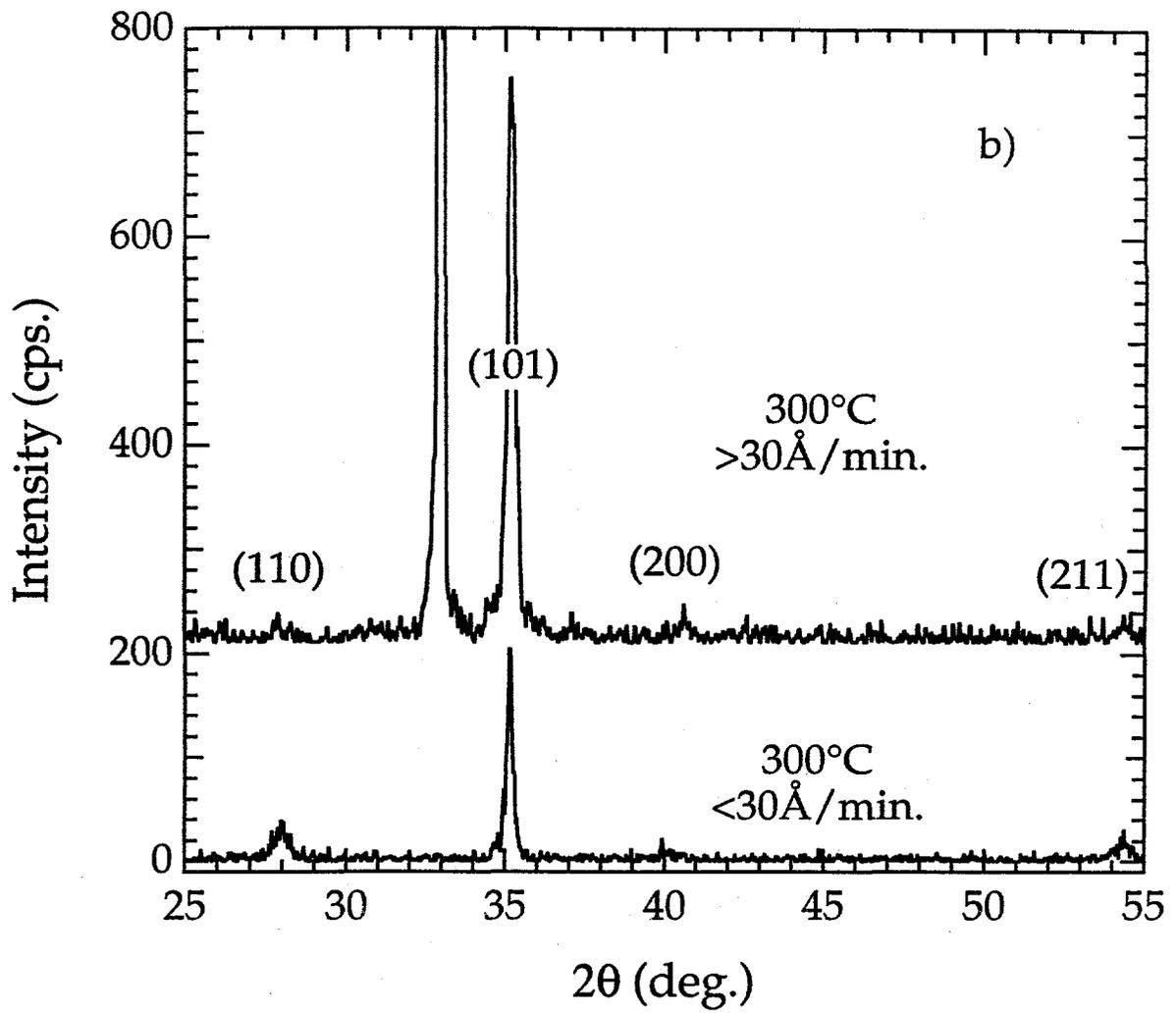


FIG. 2B

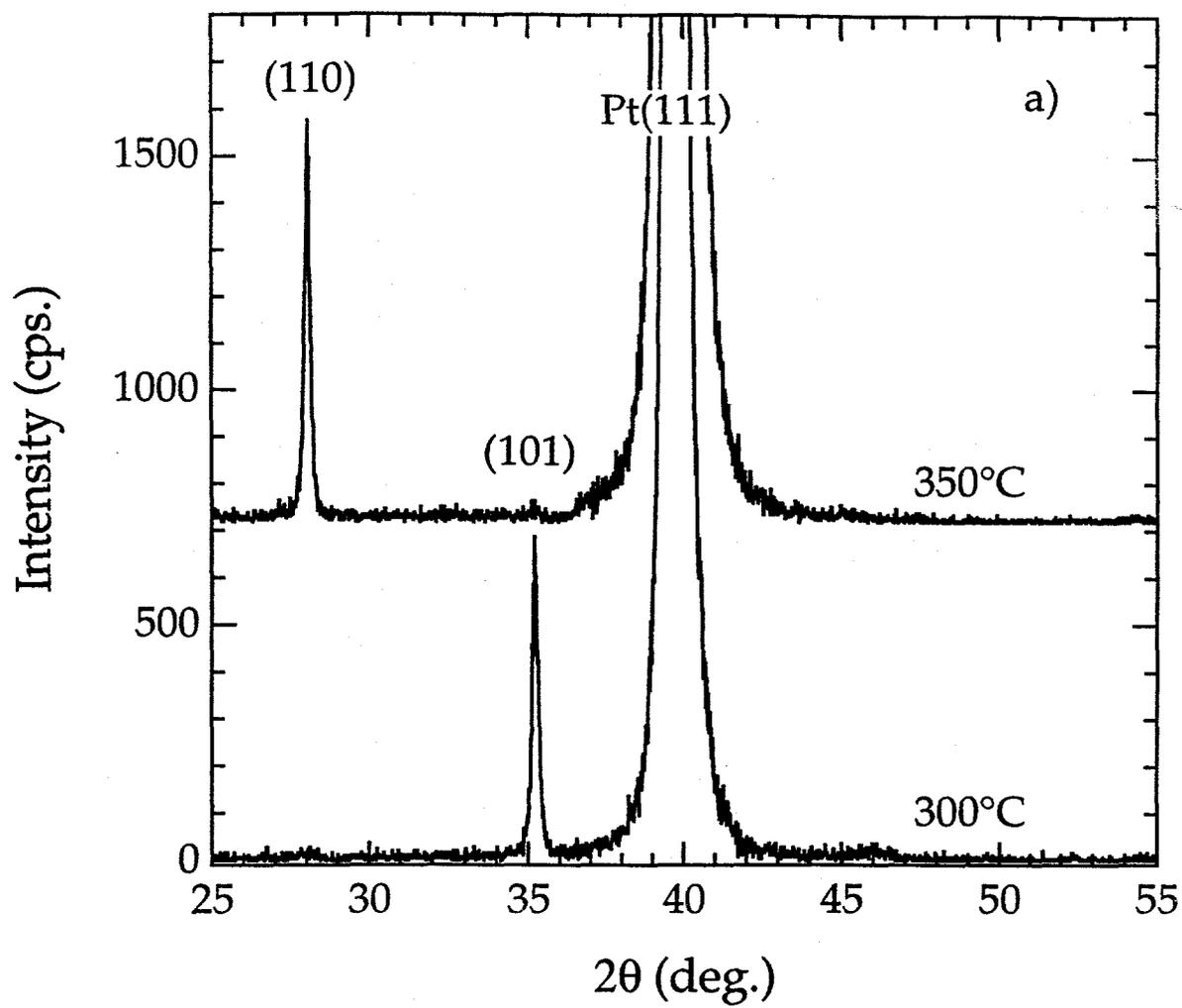


FIG. 3A

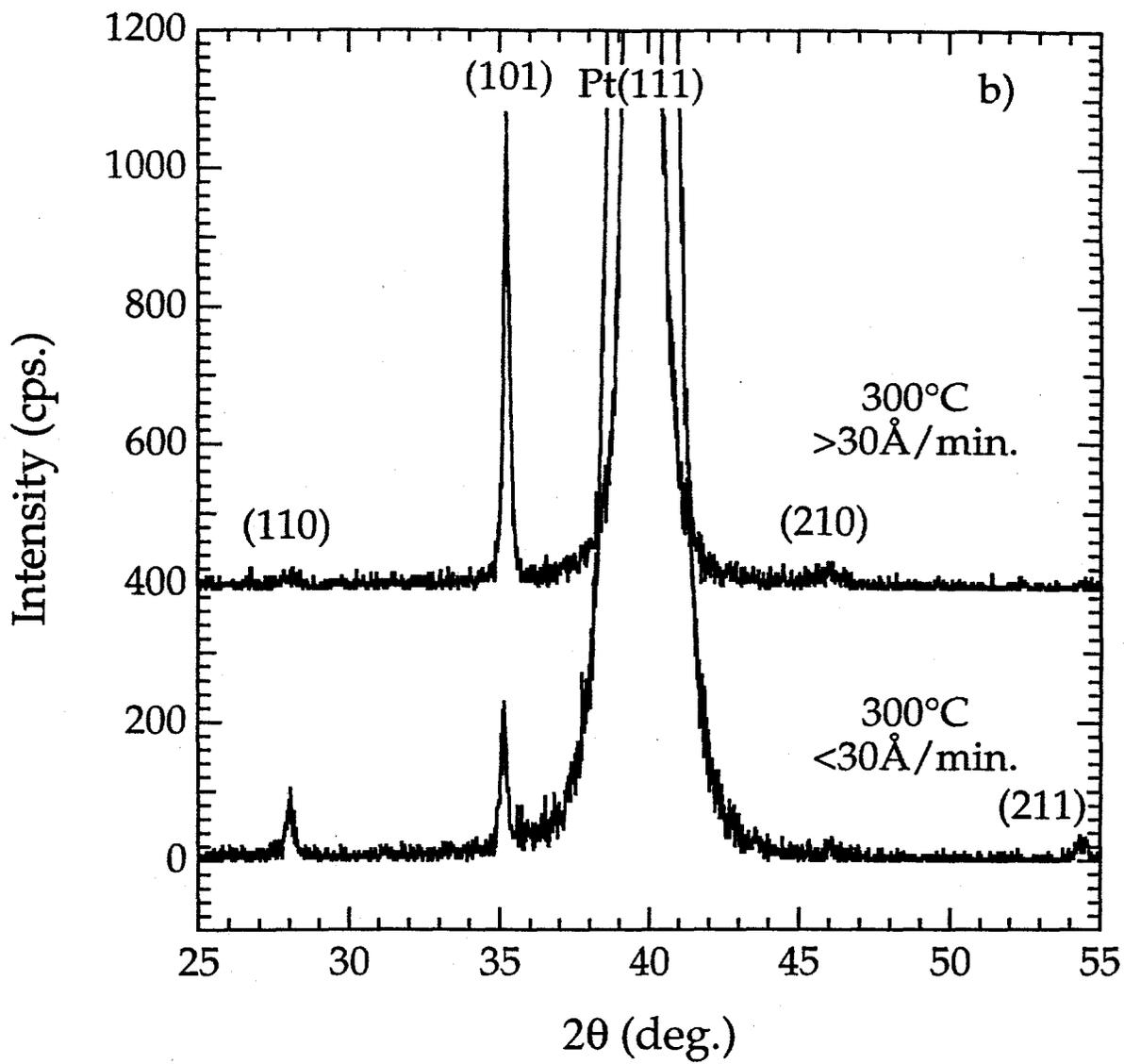
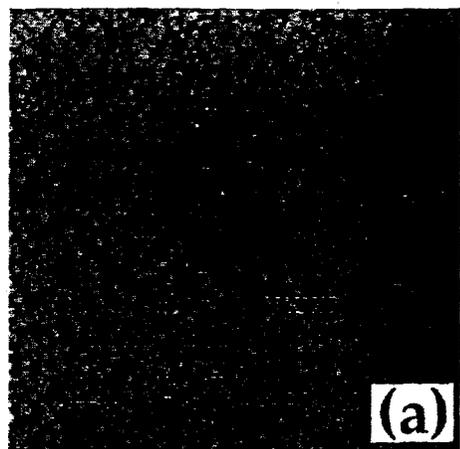


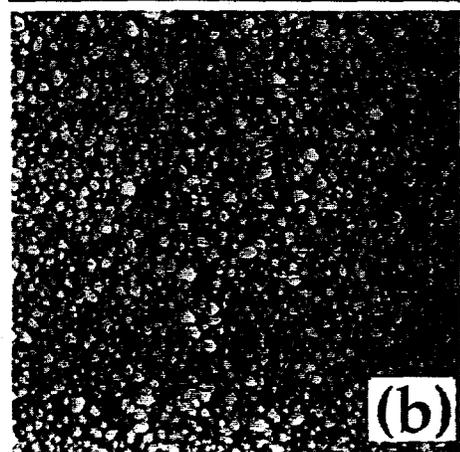
FIG 3B



75 nm



0 nm



75 nm



0 nm

5 μ m