Chapter 3

Experimental Results and Discussion of Physical Properties

3.1 Physical Properties

It should be understood that the performance of nonvolatile memory depend on the electrical properties, the yield of nonvolatile memory depend on the physical properties. In the following sections, we will introduce the physical measurements and analyses include the thermal analysis, X-ray diffraction analysis, scanning electron microscope analysis, atom force microscope analysis, transmission electron microscopy, and X-ray photoelectron spectrometer analysis. The measurements are used to see the pyrolysis temperature, crystallization temperature, preferred orientation, grain size, morphology of surface and cross-section, the surface roughness degree, the content of organic impurity, the content of major element, and the bonding energy. Besides, the physical properties measurement can help us to find the better fabrication parameters.

3.1.1 Thermal Analysis

Thermal analysis helps to find the suitable temperature for growing the high quality BTO thin film by sol-gel method. The best method to find the suitable temperature parameter is by the thermal analysis instrument. Sol-gel is a kind of chemical deposition method and we fabricate the thin film of BTO by heating the sample after spin coating

the precursor solution. In the process, the solution will evaporate and the atoms will link together to form the BTO thin film, which is pyrolysis procss. However, different pyrolysis temperature and raising rate will affect the quality and electric properties of thin film. Thermal analysis can be a good tool to find the suitable temperature. Fig. 2-5 is the thermogravimetry (TG) and differential thermogravimetry (DTG) illustrations and Fig. 2-6 is the differential thermal analysis (DTA) illustrations. From the TG and DTG illustrations, it is known that there are weight loss from 150°C to 400°C .The maximum of weight loss appear in the degree of 300°C to 400°C and keep smooth after 400°C .The DTA illustration shows that there are two main peaks. One peak is near the 200°C, the other is near the 517°C. If the straight lines were drawn from the peak, the reaction completion points are the points where the straight line separates from the peak. The points are at 200°C and 517°C. At 200°C, the solution should be evaporated. When the temperature reaches 517°C the thin film should be crystallized, and it could be verified by the illustration of XRD in Fig. 3-1.

3.1.2 XRD Analysis

The 100 nm thickness $LaNiO_3$ (LNO) buffer layer with (100) and (200) preferred orientation (Fig. 3-1) is deposited at 250°C on $Pt/Ti/SiO_2/Si$ substrate by a rf magnetron sputter system. The LNO buffer layer used here is due to the better adhesion for BTO solution during spin-coating. Fig. 3-2 shows the XRD analysis for the as deposited BTO. A series of thermal processes has been done to find the phases change in different temperature, Fig. 3-3 shows the XRD analysis in the different thermal treatment temperature. Obviously, the peak of BTO will appear after of thermal treatment temperature after 500°C. It means that the phase of BTO thin film will transform from

amorphous into crystal after 500°C thermal treatment. The high temperature will increase the degree of crystallization and shift it to higher angle. It can be observed clearly that the grain size become bigger at higher temperature. From those experimental data of XRD, there are some phenomena that can be found. The different thermal treatment temperature is higher than 500°C, the BTO thin film will be crystallized.

3.1.3 SEM Analysis

SEM is a very useful instrument to observe not only the surface but also cross-section morphology. Fig. 3-4 shows the SEM illustration of BTO thin film and the pyrolysis temperature is 400°C with three BTO layers by 0.04M solution. Fig. 3-5 shows the thickness of bottom electrode, Pt/Ti, is 96nm, and the buffer layer, LNO, is 136nm. The BTO thin films have average thickness of 43nm. To observe the surface morphology in various thermal treatment parameters, a series of SEM analysis had been done to realize it. Figure 3-6 shows BTO thin film, it was known from the illustration that the surface changed at different thermal treatments: (a)as-deposited (b)400°C (c)500°C (d)600°C (e)700°C. In addition to different thermal treatment temperature, will affect the morphology of experiment sample. When the temperature reaches 600°C the thin film should be crystallized, and it could be verified by the illustration of XRD in Figure 3-3. Figure 3-6 (a)~(e) shows the grain sizes of BTO films after 400°C annealing in N_2 were similar to those of the as deposited films. In the sample annealed at 600°C in N_2 ambient, the grain sizes of BTO films become larger and looked clearly.

3.1.4 AFM Analysis

To investigate the effect of annealing temperature on the surface roughness of BTO films, we check the BTO films annealed at various temperatures by AFM. Figure 3-7(a), (b), (c), (d) and (e) show the r.m.s surface roughness of BTO thin films deposited at 400°C with various thermal treatment temperature in N2, 1hr ambient (a)as-deposited (b)400°C (c)500°C (d)600°C (e)700°C. From Figure 3-7, the crystallinity of BTO films are improved by high annealing temperature but high surface roughness is indicated due to grain growth for BTO films annealed at high temperature. The mean roughnesses of BTO annealed at as-deposited, 400, 500, 600 and 700°C in N2 ambient are 1.676, 2.029, 2.344, 2.813 and 3.233 nm, respectively, as show in Figure3-8 and Figure3-9 The higher surface roughness may result in higher leakage current and the crystallinity can affect the leakage current, too.

3.1.5 TEM Analysis

Figure 3-10 shows the field emission transmission electron microscopy (TEM) image of the BTO/LNO/Pt/Ti/SiO2/Si. Moreover, the crystal structure and the compositions of the BTO thin film were also identified by the selected area electron diffraction (SAED) and the Energy dispersive X-ray analyzer (EDS), respectively. From the SAED results, the BTO thin film is amorphous (not show here), which is the same results characterized by x-ray diffraction pattern analysis as shown in Figure 3-2 From the EDS results, the atomic ratio of BTO thin film is found to be about 1 : 4 :10. The ultra-thin film layer and its interface qualities was investigated with the Philips JEOL JEM9100 Transmission Electron Microscopy, the thickness of bottom electrode, Pt/Ti is 80/20nm, LNO is 120nm and the BTO thin film average thickness for one layer is 20nm.

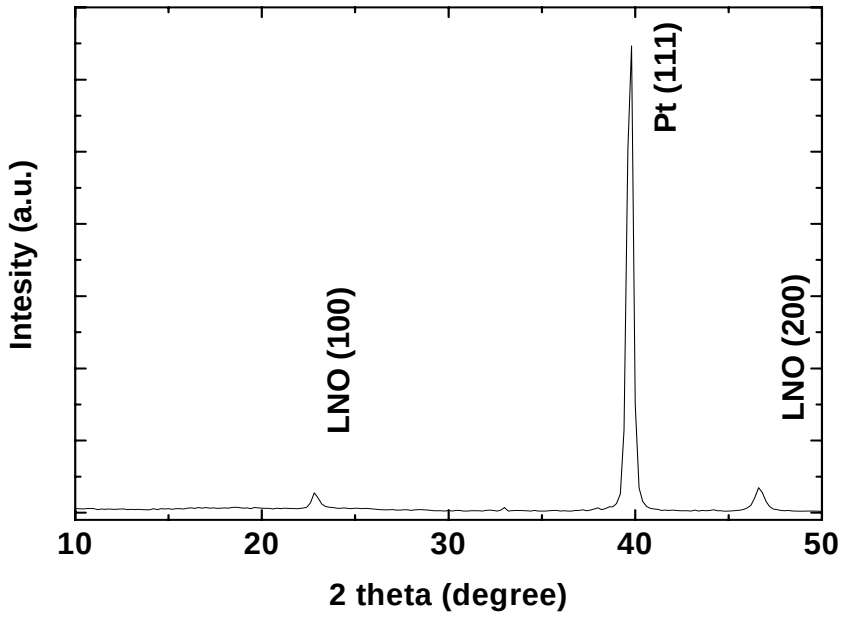


Fig.3-1 XRD pattern of LNO/Pt/Ti bottom electrode

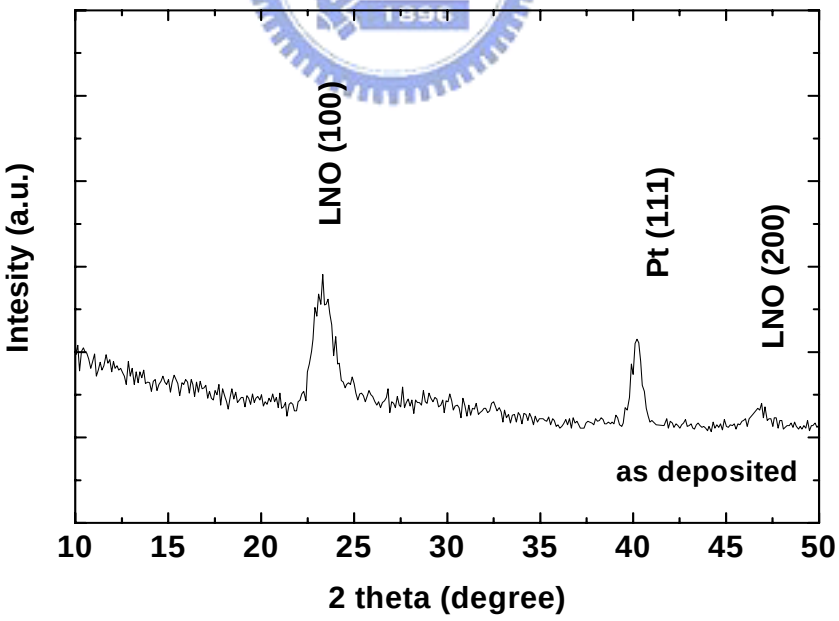


Fig. 3-2 XRD pattern of as deposited BTO thin film

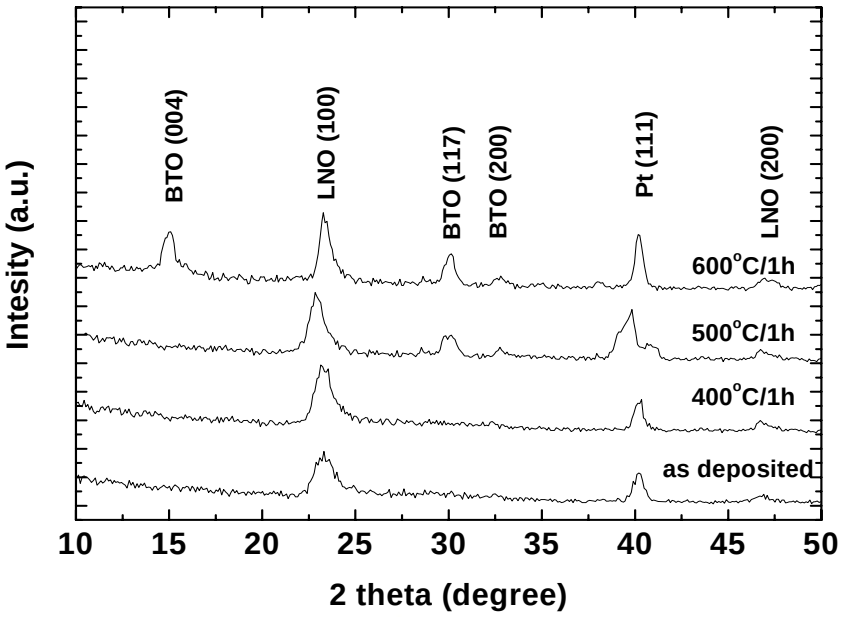


Fig. 3-3 XRD pattern of BTO will thermal treatment after 600°C

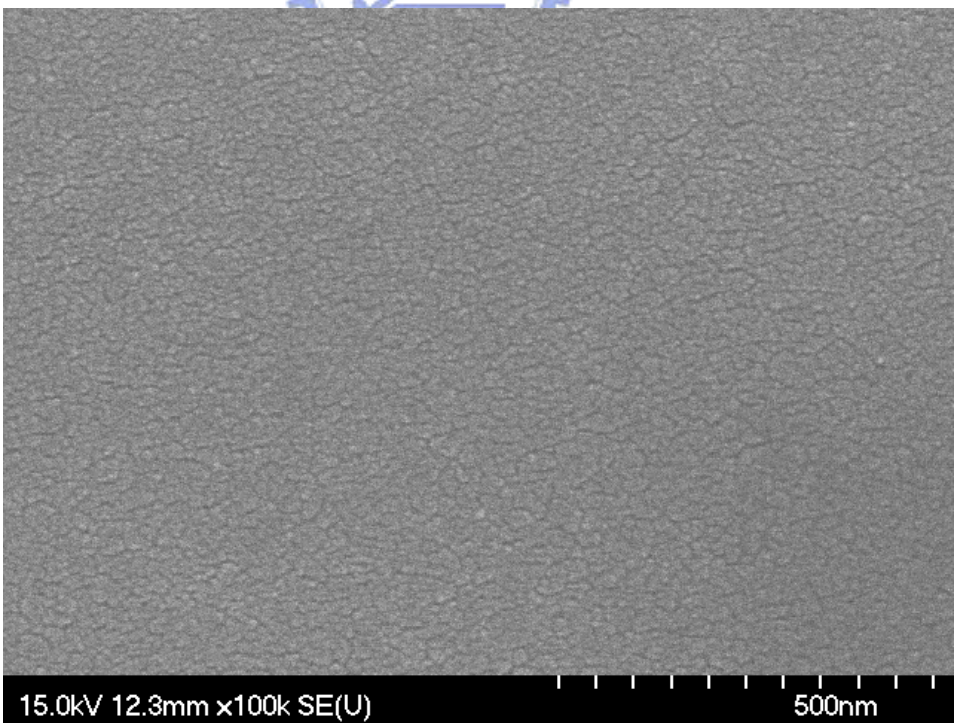


Fig. 3-4 The surface of BTO thin film pyrolysis at 400°C with 3layers on LNO substrate

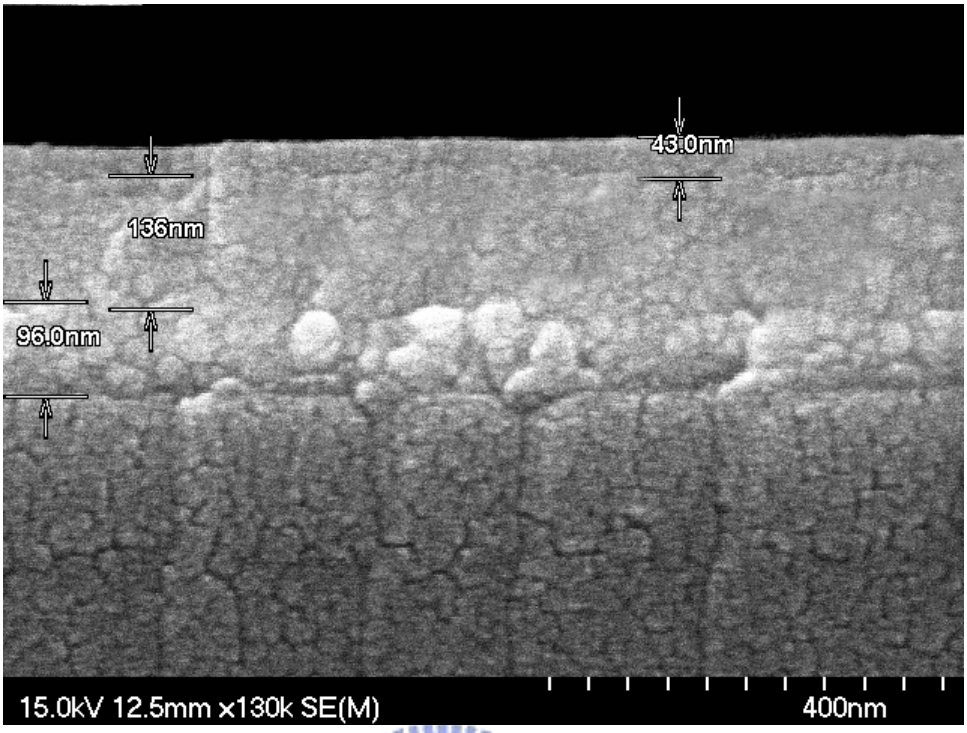
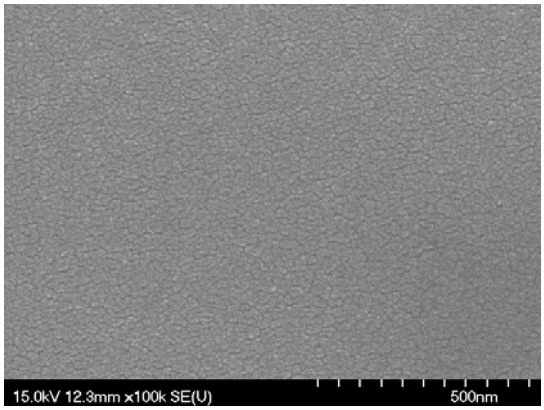
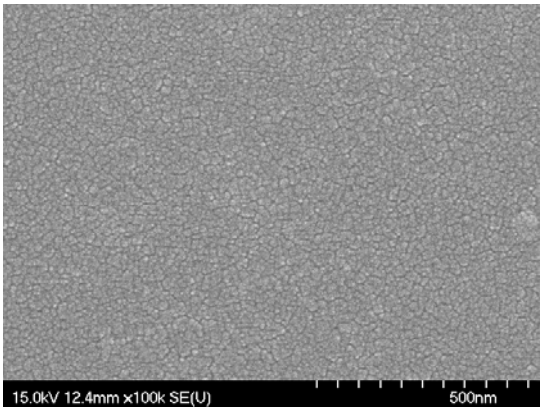


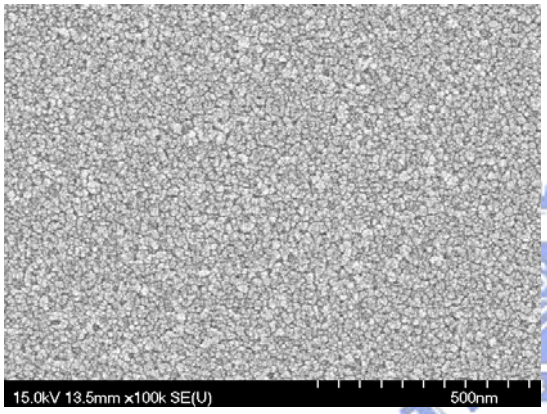
Fig. 3-5 The cross-section of BTO thin film with 3layers on LNO/Pt/Ti substrate



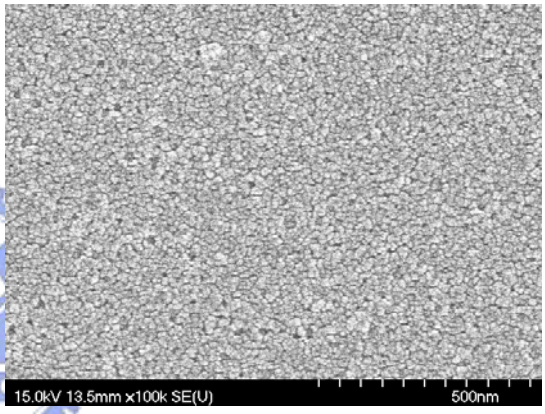
(a) as-deposited



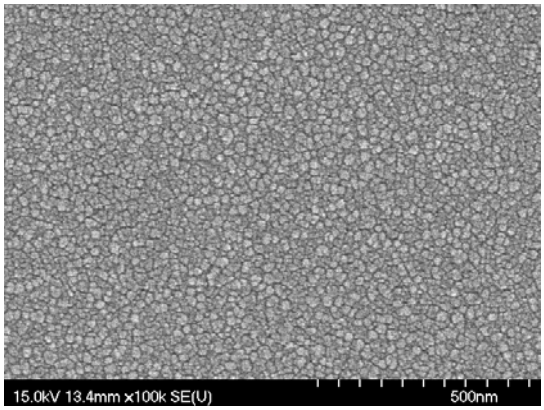
(b) thermal treatment at 400°C 1hr in N_2



(c) thermal treatment at 500°C 1hr in N_2

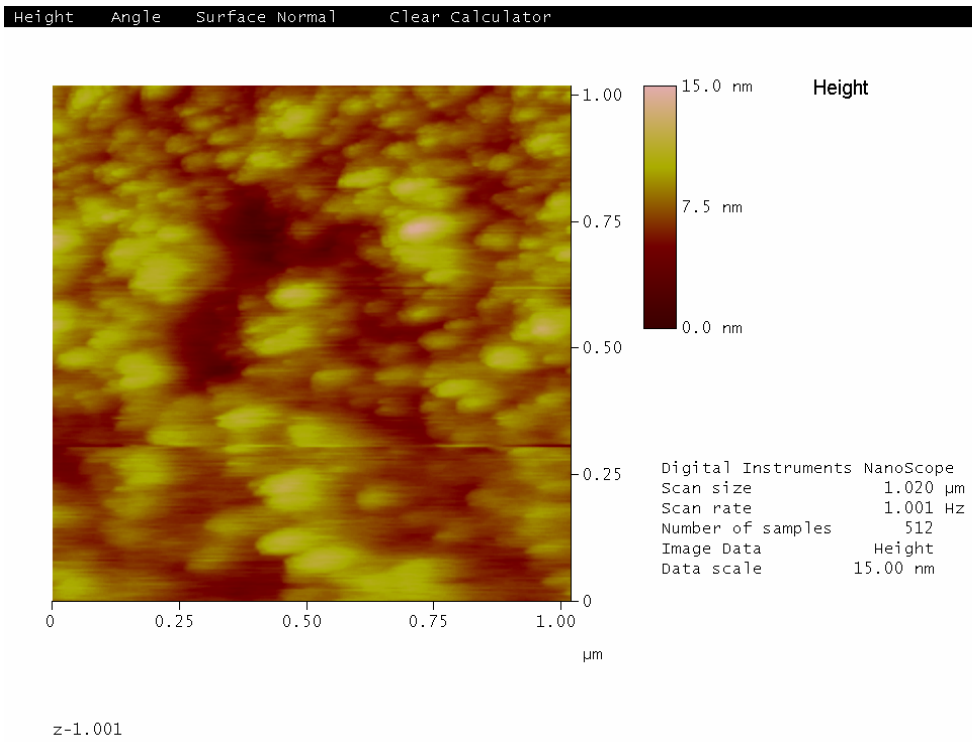


(d) thermal treatment at 600°C 1hr in N_2

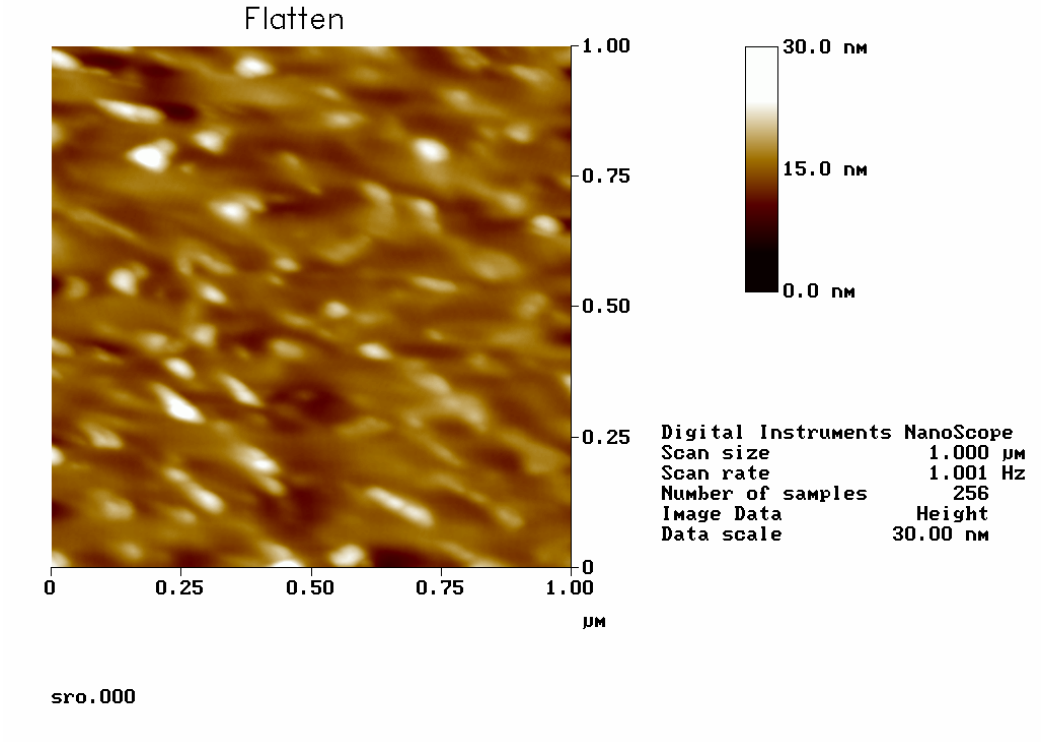


(e) thermal treatment at 700°C 1hr in N_2

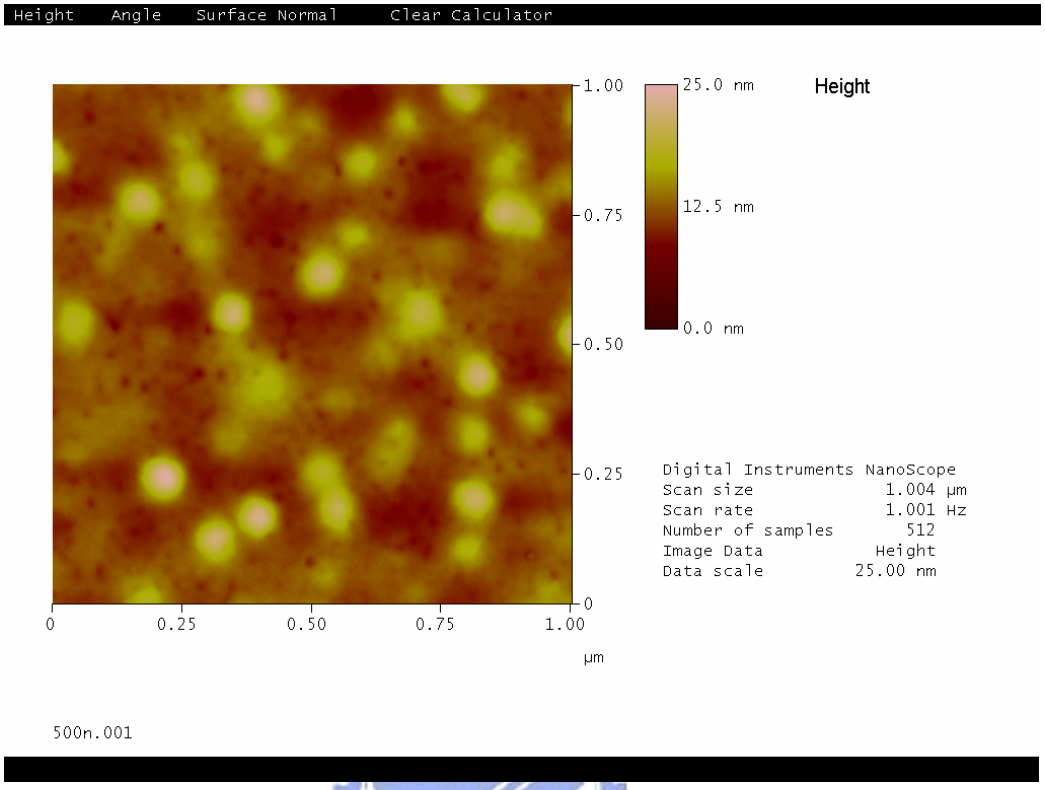
Fig. 3-6 SEM of BTO thin film at different thermal treatment temperature



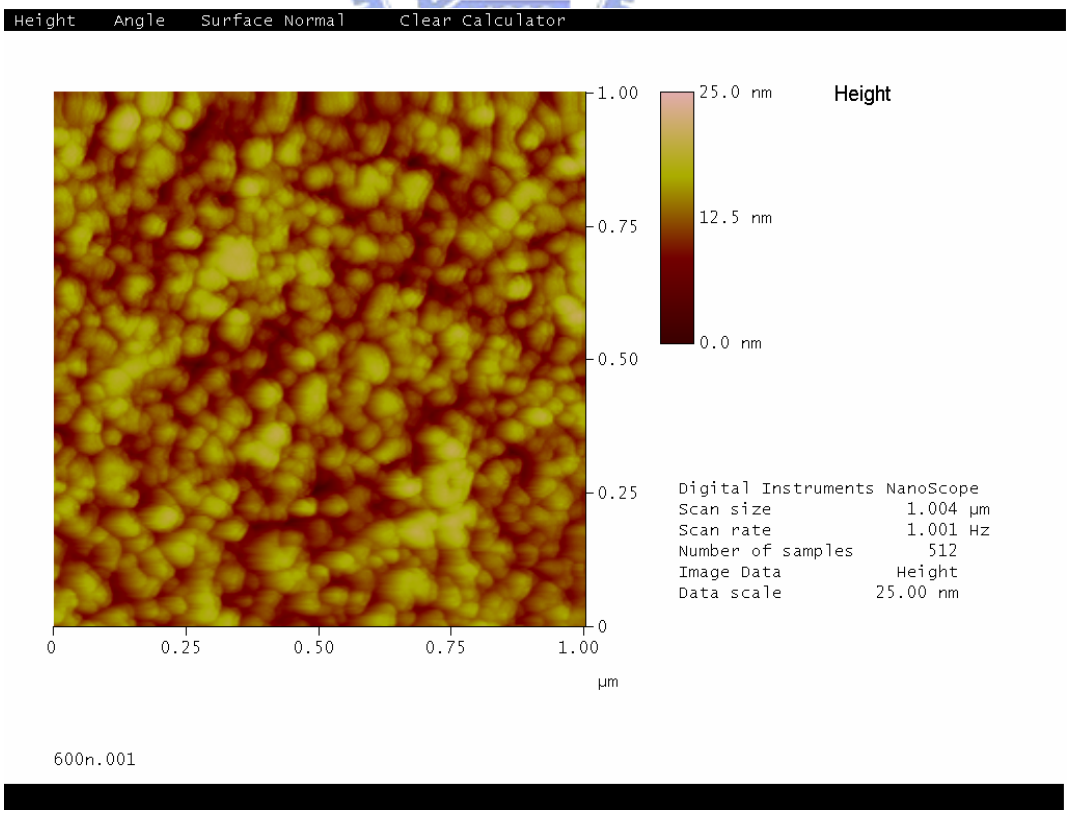
(a) as-deposited



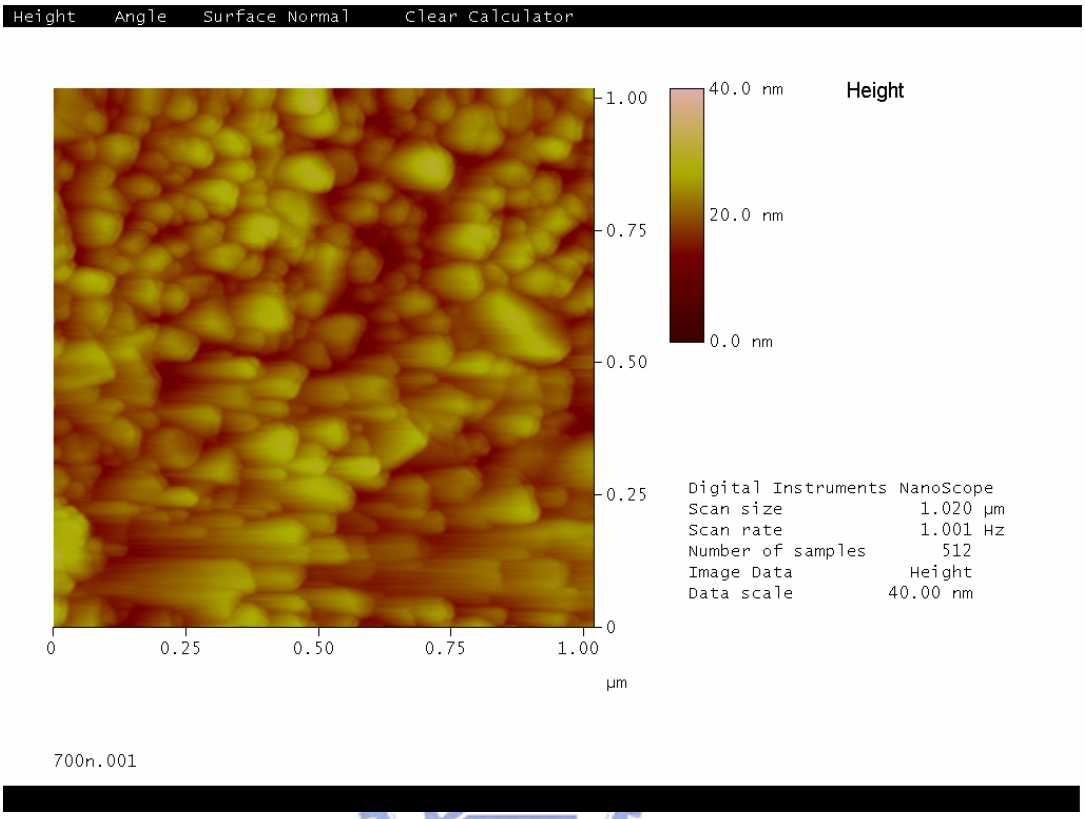
(b) thermal treatment at 400°C 1hr in N_2



(c) thermal treatment at 500°C 1hr in N_2



(d) thermal treatment at 600°C 1hr in N_2

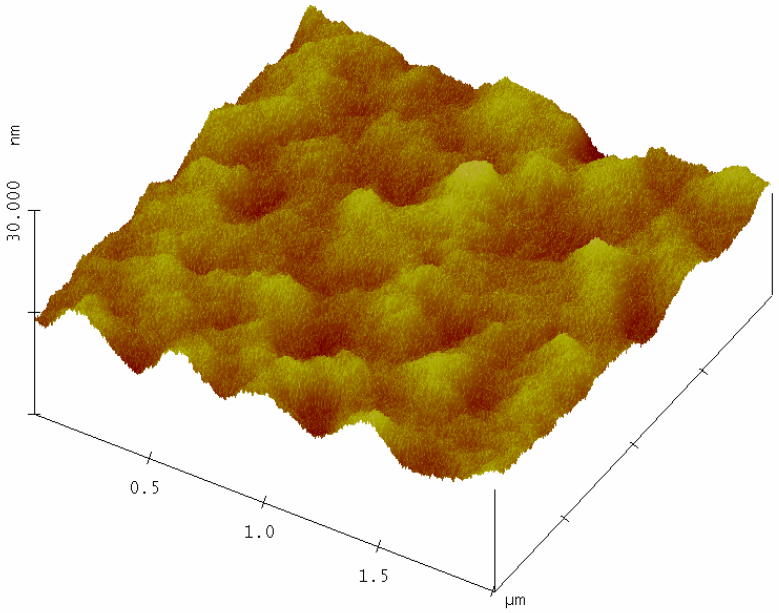


(e) thermal treatment at 700°C 1hr in N_2

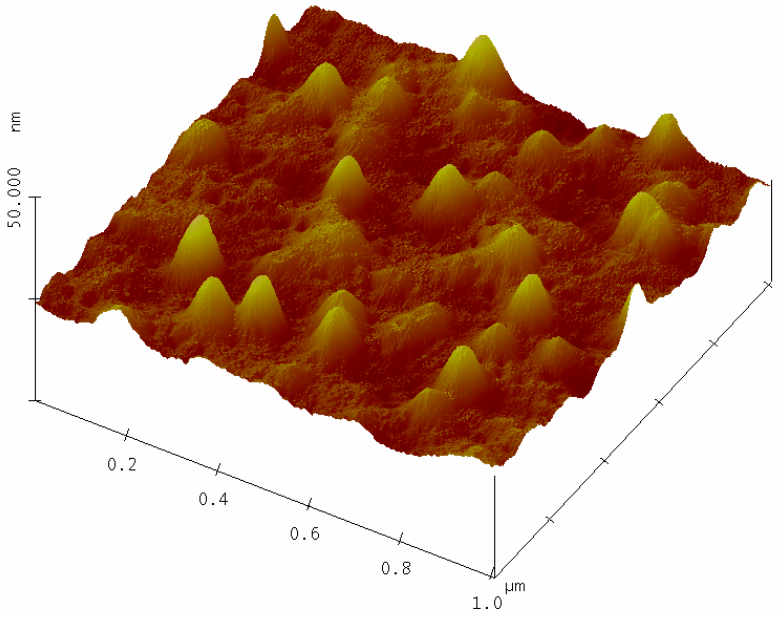
Fig. 3-7 AFM of BTO thin film at various thermal treatment temperatures

	Ra	RMS
as-deposited	1.320 nm	1.676 nm
400 ^{o}C	1.497nm	2.029nm
500 ^{o}C	1.722 nm	2.344 nm
600 ^{o}C	2.353 nm	2.813 nm
700 ^{o}C	2.596 nm	3.233 nm

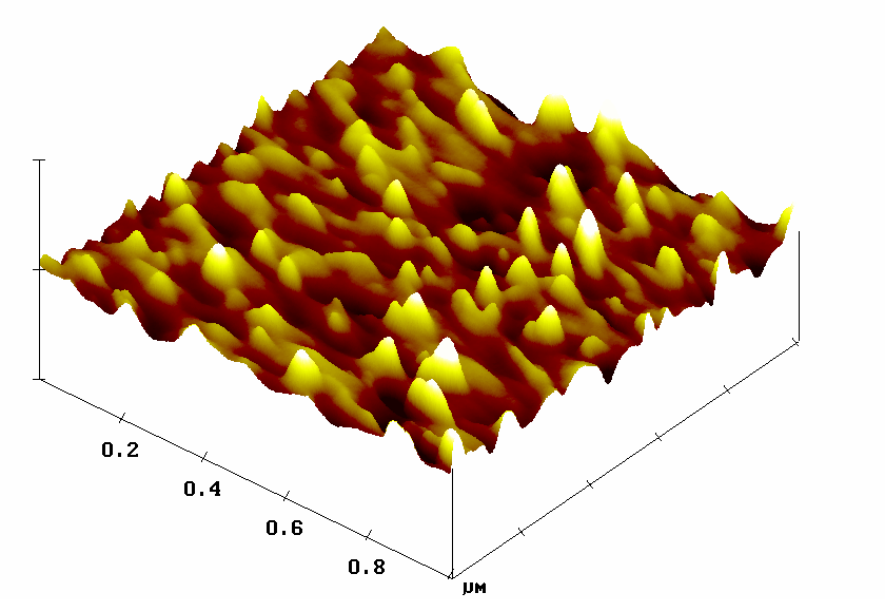
Table 3-1 Surface roughness analysis of BTO thin films



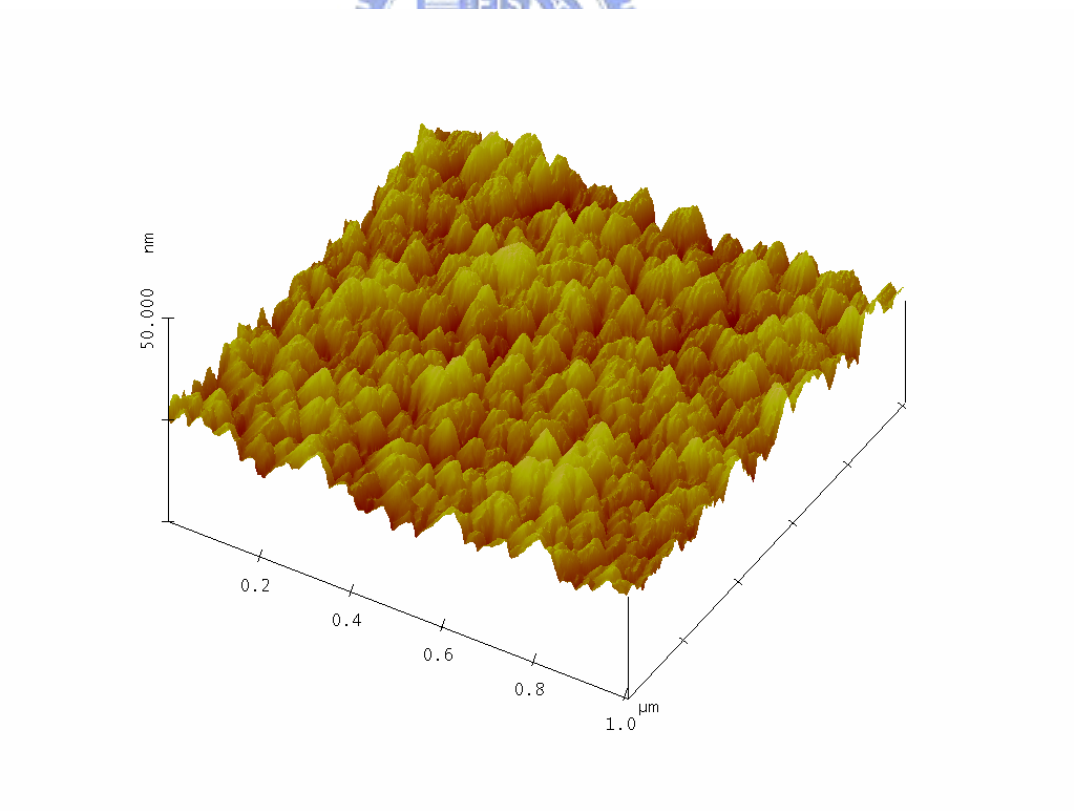
(a) as-deposited



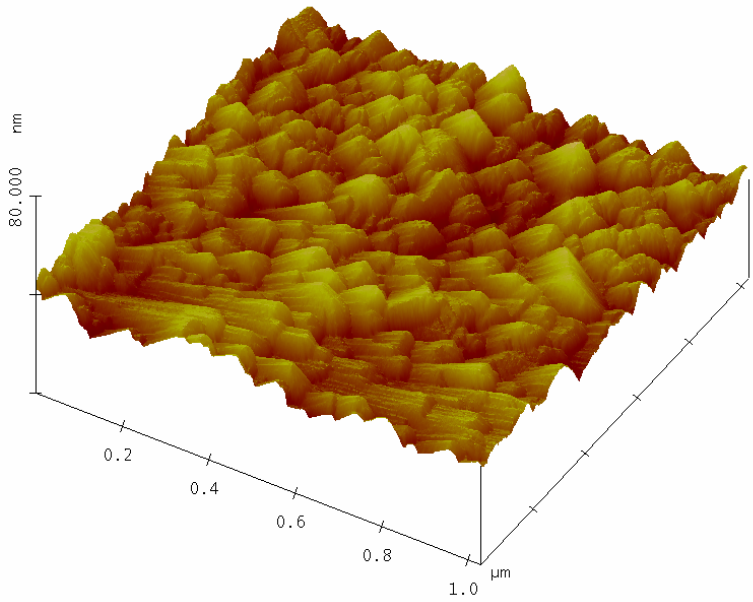
(b) thermal treatment at 400°C 1hr in N_2



(c) thermal treatment at 500°C 1hr in N_2



(d) thermal treatment at 600°C 1hr in N_2



(e) thermal treatment at 700°C 1hr in N_2

Fig. 3-8 The diagrams of r.m.s surface roughness of BTO thin film witch various thermal treatment temperature in N_2 ambient

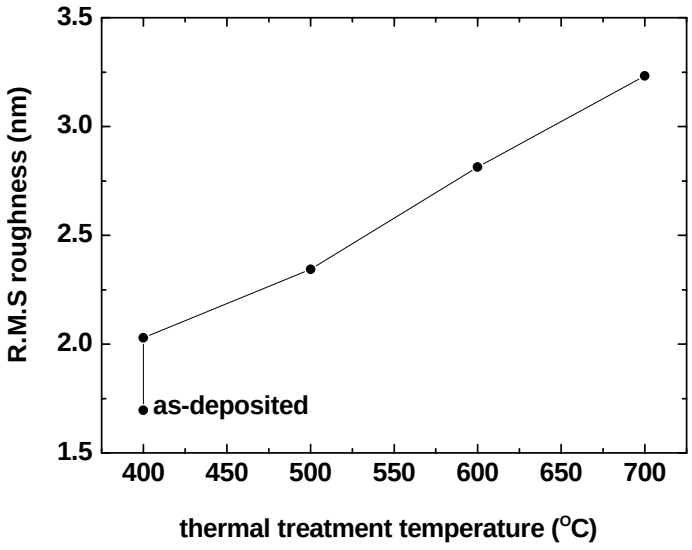


Fig. 3-9 The variation in R.M.S surface roughness of BTO thin film with various thermal treatment temperatures in N_2 ambient

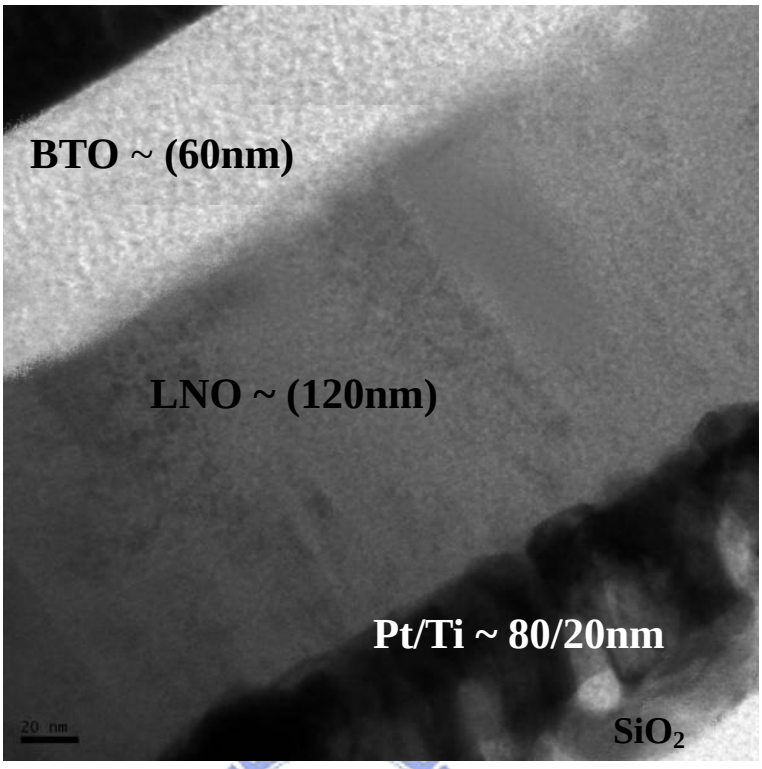


Fig. 3-10 Field emission TEM image of BTO/LNO/Pt/Ti structure on SiO_2/Si