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Full Length Research Paper

The growth of thin Titanium oxide (TiO_2) film and nano size TiO_2 powder

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The growth of thin films of TiO_2 directly on Si surfaces is studied with Auger Electron Spectroscopy. The information from these studies about the titanium oxide properties and the changes of the electronic structure is enhanced by the use of sol-gel method for synthesizing nano-size TiO_2 powder. The obtained results show that titanium oxide with higher dielectric constant and amorphous structure can be as a good gate dielectric for the future of CMOS (Complementary- Metal- Oxide- Semiconductor) devices.

Key words: Thin film, nano transistor, TiO_2 and sol-gel method.

INTRODUCTION

Future high performance devices for higher speed and lower power consumption would require active device dimensions in the sub- 100 nm regime. Some issues such as leakage current, tunneling current and Boron diffusion through the ultra thin silicon dioxide as a gate dielectric of current CMOS make. Actually, as the dimensions of electronics devices arte scaled down, the high electron tunneling rates in the ultra thin gate oxides is becoming an increasingly critical problem. The materials properties of alternative higher- k dielectrics are therefore attracting increasing attention. Metal-oxide with high dielectric constants have the potential to extend scaling of transistor gate capacitance beyond that of silicon dioxide. TiO_2 is a material that is under active consideration in different places [Anderson, 2003; Sikka et al., 1982; Casillas et al., 1994; Ju et al., 2007; Bahari et al., 2006; Morgen et al., 2007; Bahari et al., 2008] and is now attracting the attention of the device community [Kim et al., 1999; Ding et al., 2000; Yang et al., 2001; Iwamoto et al., 2001]. It is also a popular photo catalyst and is used in the manufacture of optoelectronics. Another area where TiO_2 will become of use is as dielectric films in cell capacitors of dynamic random access memory (DRAM). There, nano-particle titanium can be introduced as a storage electrode, forming a capacitor with a metal-TiO_2-silicon structure. The use of titanium for the storage electrode has been proposed to eliminate interfacial oxide growth. In fact, engineers are doubt to use high-k dielectric on silicon substrate due to formation of unwanted layer between TiO_2 and Si layers. In the present work, we have demonstrated series of experiments to grow thin TiO_2 film and synthesize nano size titanium particles as good nano transistor elements.

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EXPERIMENTAL PROCEDURES AND DETAILS

Mirror-polished n-type Si (100) samples were used as substrates. These wafers were cut into $3 \times 1 \times 0.2 \ cm^3$ and then silicon samples introduced in the UHV (Ultra High Vacuum) chamber after a rinse with ethanol in an ultrasonic bath. The chamber was then baked before the experiments begin. After baking the background pressure was $2 \times 10^{-10} \ Torr$. Of course, the pressure inside the vacuum chamber increasing during the oxide and nitride growth on silicon substrate. All further cleaning was done inside the UHV chamber by heating with a direct current through the sample, initially up to 1200 ^{0}C and then at higher temperatures to restore a clean Si surface. Earlier measurements which a residual gas mass spectrometer in the line of the beam has shown a very high proportion (about 50%) of the oxygen and nitrogen which are produced with this setup. Typical total pressures in the chamber during exposure were around $2 \times 10^{-10} \ Torr$. The Si structures are kept at room temperature. Referring to our recent works [Casillas et al., 1994; Ding et al. 2000], the XPS spectra of oxide and nitride are shown in Figure 1. We can also distinguish two different thickness oxide and nitride films on these substrates by

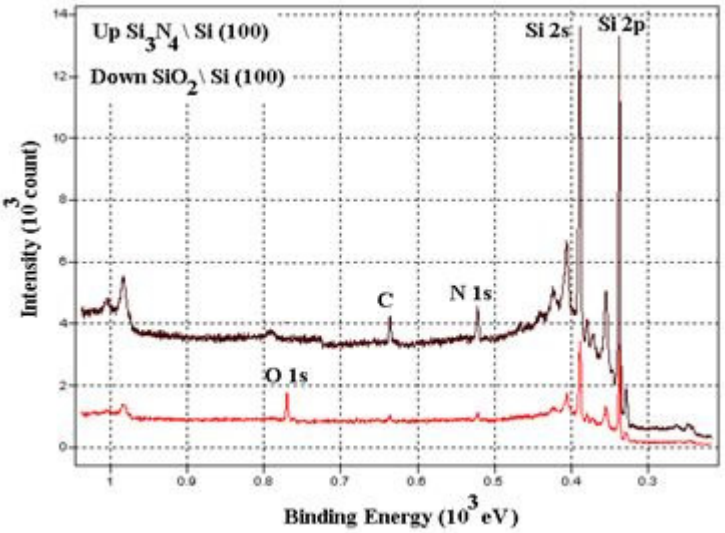

Figure 1. XPS spectra of SiOxNy on Si (100) at 600°C (Nitrogen exposing time: 10 and 20 min).

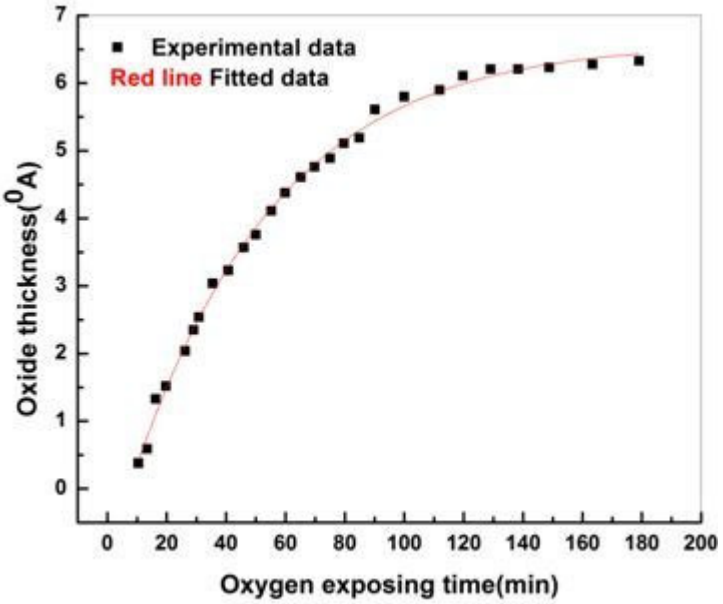

Figure 2. Isothermal plasma oxidation and saturation growth of a uniform oxide on Si (100) 2×1 at 500°C and $5\times10^{-9}Torr$.

looking at Figures 2 and 3.It is clear that the growth of silicon oxide and silicon-nitride on Si (100) have Boltzmann behavior. Titania is known to have three natural polymorphs, that is rutile, anatase, and brookite. Only anatase is generally accepted to have significant photocatalytic activity. Titania can be synthesized by various techniques, such as precipitation [Kim et al., 1999], chemical vapor deposition [Ding et al., 2000], hydrothermal method [Yang et al., 2001] and glycothermal method [Iwamoto et al., 2001]. Another common technique that can result in titania with extremely high surface area is sol–gel method. The sol-gel process is commonly applied to synthesis such TiO_2 materials owing to its several advantages such as low temperature processing and the ability to prepare materials in various shapes, compared with the conventional preparation procedures of glass and ceramics [Kato et al., 1994; Abe et al., 1988]. In this work we prepare TiO_2 by using hydrolysis procedure of $TiCl_4$ which is transformed to anatase by heating it at 300, 500 and 700°C. It obviously depends on the preparation procedures and TiO_2 content in combination. Anatase is generally transformed to rutile if calcinations temperature and TiO_2 content increase. By adding more SiO_2 to TiO_2, the obtained

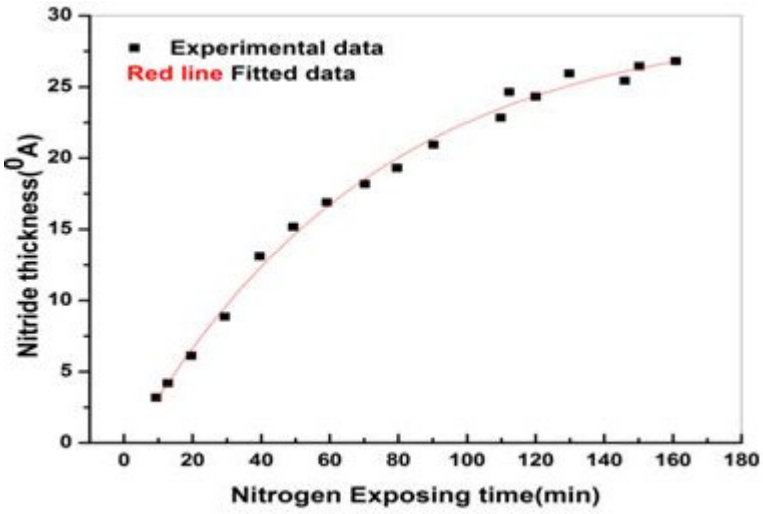

Figure 3. Isothermal. Isothermal plasma nitridation and saturation growth of a uniform nitride on Si (100) 2×1 at 500℃ and $5\times10^{-9}Torr$.

Table 1. Materials and corresponding molar ratio.

Materials	TEOS	$TiCl_4$	Ethanol	H_2O	CH_3COOH
Symbol	A	B	C	D	E
Molar ratio	A	B	7(A+B)	10(A+B)	2(A+B)

powder trend to crystalline structure (Table 1).

The preparation of TiO_2-SiO_2 gel is below, such that Tetraethyl-Orthosilicate (TEOS) (Merk, ≥ 99) was hydrolyzed with di-ionized water in that ethanol. Ethanol acts as a mutual solvent. TEOS, in ethanol was hydrolyzed with water containing acetic asid at room temperature for 30 min. The solution was then mixed with titanium chloride $TiCl_4$ (Merk, ≥ 99 at 0℃ in specific molar ratio to obtain various content of TiO_2. After 30 min stirring at room temperature, the sol was vibrated for 20 min in ultrasonic bath to deconglomerate particles and then relaxed at room temperature for 30 min. The sol was stirred at 60℃ until it become gel and removes ethanol (about 24 h). After gelation, samples were dried at 60℃ to remove water and acetic acid and leave a white to light yellow lump depend on TiO_2 content. After that the lump samples were milled with mortar and calcinated in 300, 700 and 900℃. The thermal gradient during experiments procedure was $5\frac{deg}{min}$ and the samples were put in oven during 2 h at calcination temperature stated above. The procedure was shown in Figure 4.

The weight percent of ingredient in production was obtained by using XRF (model: ARL 8680 S Switsland) technique and given in Table 2. The composition, structure and surface morphology of the TiO_2- SiO_2 powder were investigated by XRF, XRD, FT.IR (Fourier Transform Infrared absorption), XPS and AES.

DISCUSSION

The most noted properties of titanium oxide and titanium are their excellent resistance to corrosion which can protect the ultra high vacuum chamber and CNTFET(Carbon Nano Tube Filed Effect Transistor) as well. It is widely distributed and occurs primarily in the minerals anatase, brookite, ilmenite, pervsite, rutile, titanate (sphene), as well in many iron ores. Of these, only rutile and anatase any economic importance, yet even they are difficult to final in high concentrations. For this purpose, nano sized TiO_2-SiO_2 sols are prepared with modified sol-gel method using reduction agent. In parallel, thin titanium oxide films are grown on Si (100) substrate. Their structural properties are investigated by XRD, FT-IR, AES techniques and x-powder method, both anatase and rutile are simultaneously formed [Figures 5 and 6] since 500℃ and the complete crystallization is attainedstarting600℃. This behavior is attained thanks to the low and close activation energy of the amorphous TiO_2 to α-TiO_2 transformations. It is clear that by increasing the temperature, the intensity of peaks in XRD patterns increase and crystallization are observable. Samples with TiO_2 content above 44% have rutile and anatase phases together whereas samples with lower content have only anatase phase. Figures 5 to 10 show that, by increasing the TiO_2 content, rutile percent in mixture is explicit more than anatase and the particle size grows by increasing the calcination temperature as shown

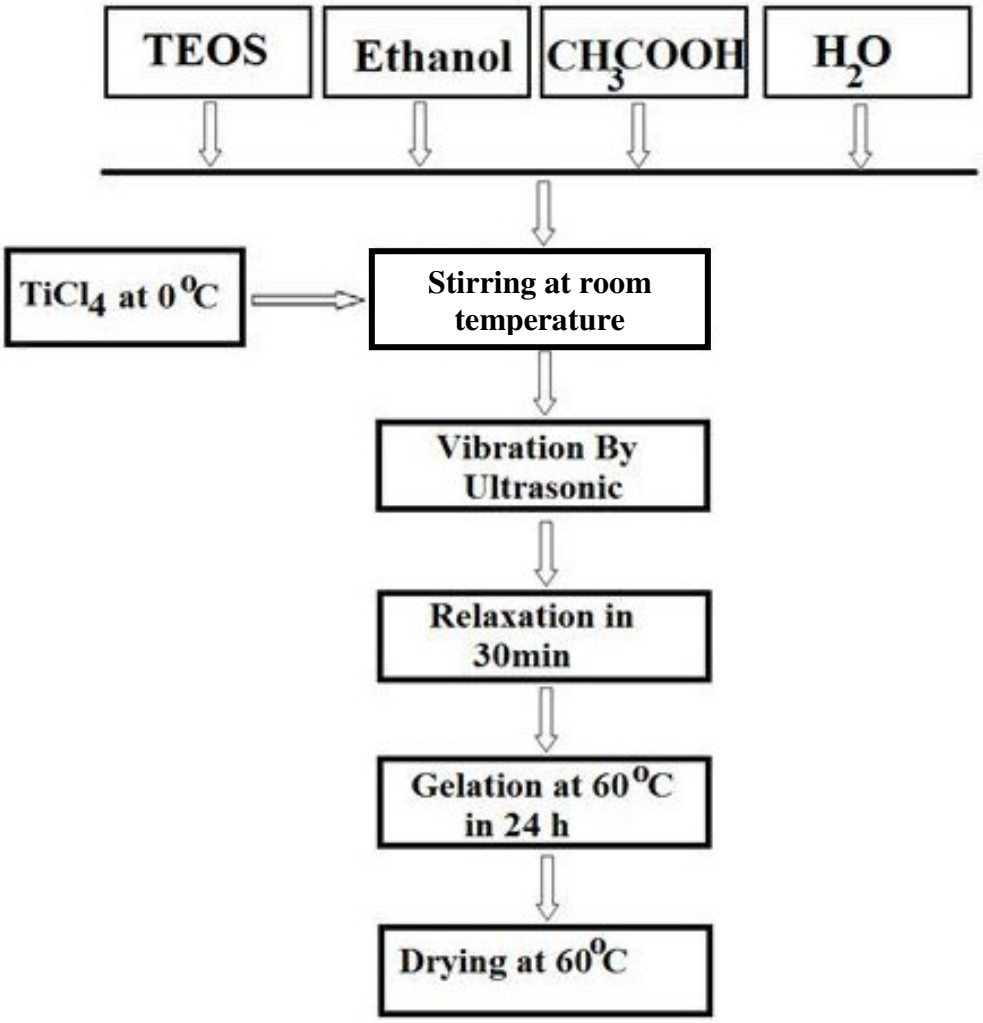

Figure 4. The procedure for preparing TiO_2-SiO_2 in mixture.

Table 2. The result of XRF analysis.

Sample	Weight percent
100	70.75%TiO_2-29.25%SiO_2
200	59.43%TiO_2-40.57%SiO_2
300	54.94%TiO_2-45.06%SiO_2
400	44.1%TiO_2-55.90%SiO_2
500	33.88%TiO_2-66.12%SiO_2
600	31.76%TiO_2-68.24%SiO_2

in Figure 11 (for thermally growth of TiO_2) and Table 3. (nano sized particles at the sol preparation, do not involve any foreign other than C and H that oxidize easily to CO and H_2O, facilitating the ionic diffusion necessary for the crystallization process. The prepared sol and thermal growth experienced linear and self-limiting growth as shown in Table 2 and Figure 4 that allows getting more rutile crystalline structure and titanium oxide amorphous. In addition, to the powder synthesis, the CVD technique is successfully used to deposit homogeneous and crack-free α-TiO_2 thin film on Si(100) substrate.

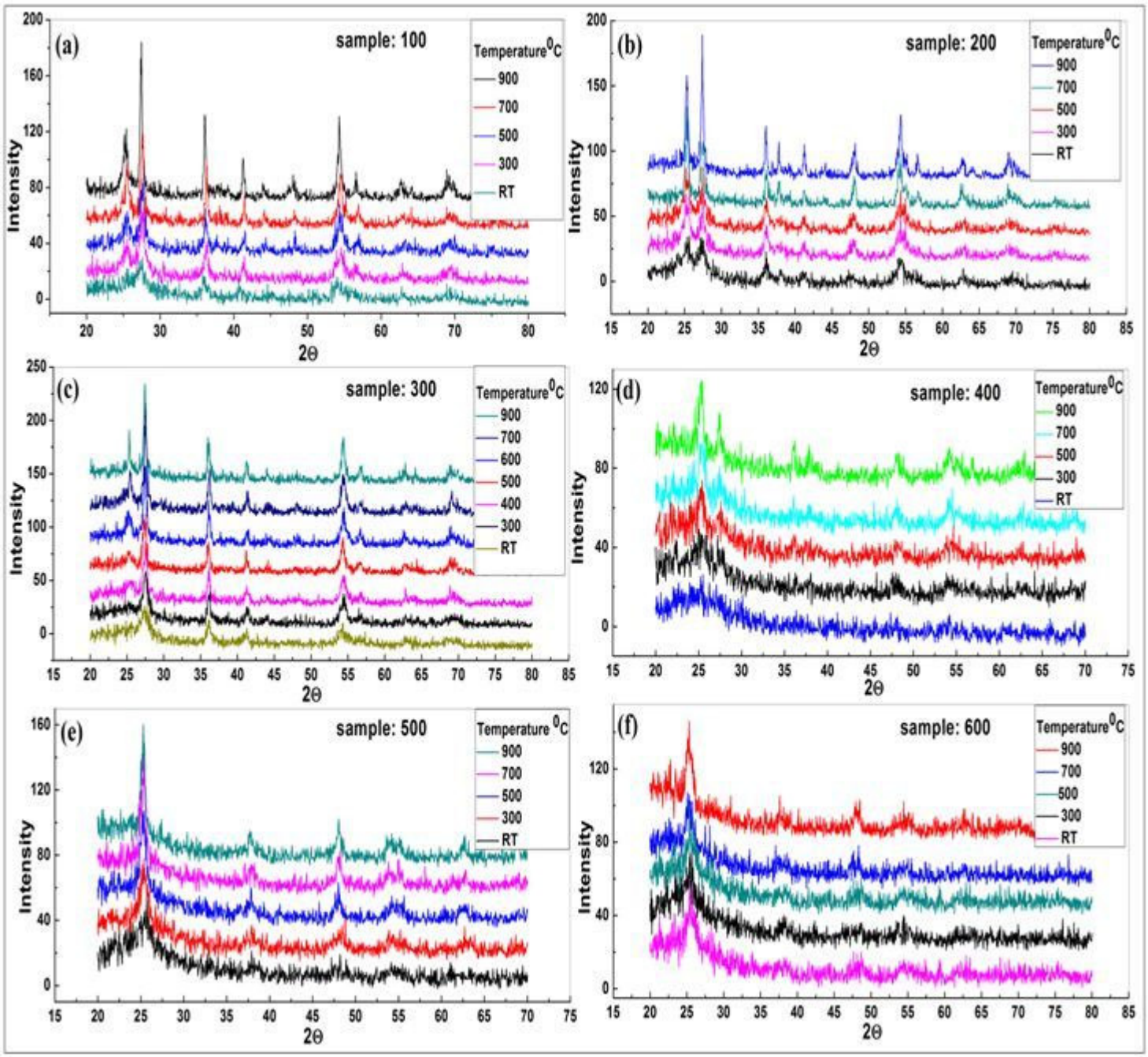

Figure 5. XRD patterns of the SiO_2 - TiO_2 powder correspond to content in table 2. at different calcination temperature. The inset table shows calcinations temperature.

The FT-IR spectrum of TiO_2-SiO_2 is shown in the Figures 12 and 13. It consists of several bands at 1740, 1630, 1060 to 1220, 950, 798 and 650 to 740 cm^{-1}. The peaks in the spectra have been assigned according to the literature [Yu and Wang, 2000].

The band at 1630 and 3300 cm^{-1} (for resolution in 400 to 2000 cm^{-1} range and 3300 cm^{-1} are not appear in spectra) are assigned to OH bending and stretching vibrations respectively. It can be ascribed to the stretching of silanol groups interacting through hydrogen bonds with water molecules. The vibration in the range 1060 to 1220 cm^{-1} is assignable to Si-O-Si vibration mode of isolated Si-OH groups. The absorption band about 1070 cm^{-1} represents the characteristic bonds of Si-O-Si

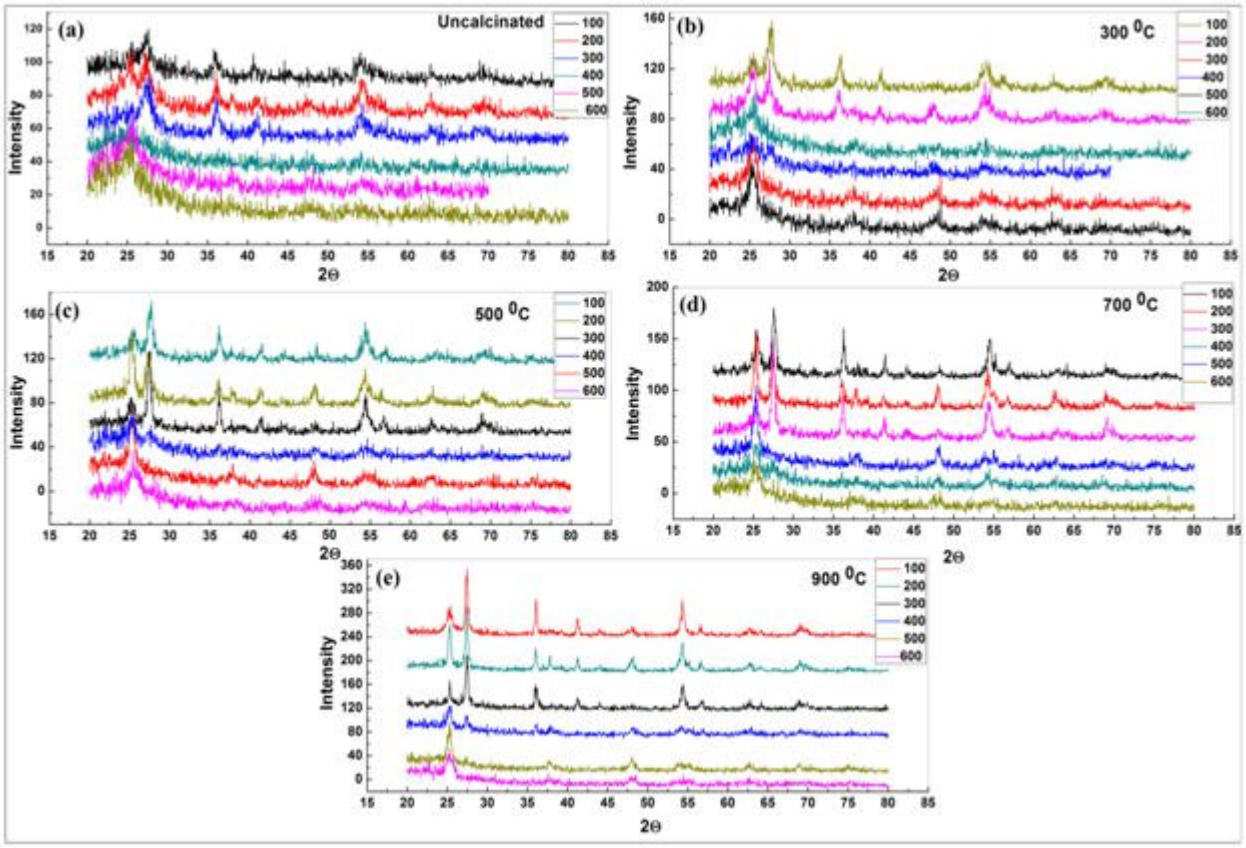

Figure 6. XRD patterns at fixed calcination temperature but different content. The inset table show sample number that has specific TiO_2 content.

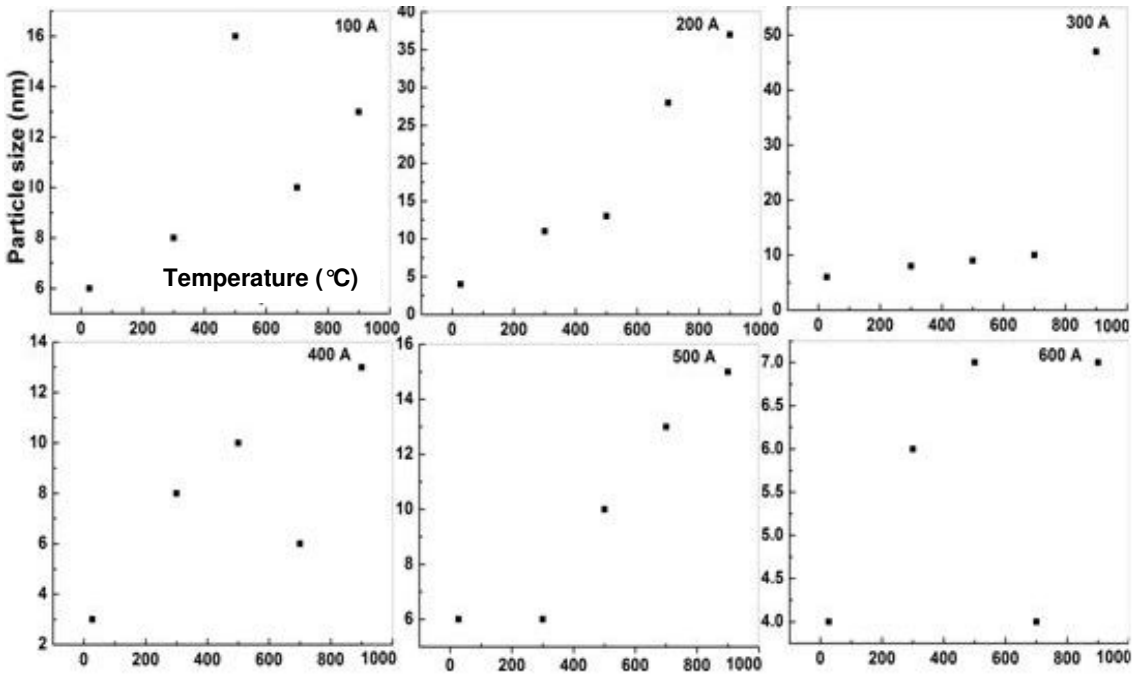

Figure 7. The size of TiO_2 particles were calculated by Scherer's equation, A=Anatase and numbers (from 100 to 600) is corresponding to Table 2.

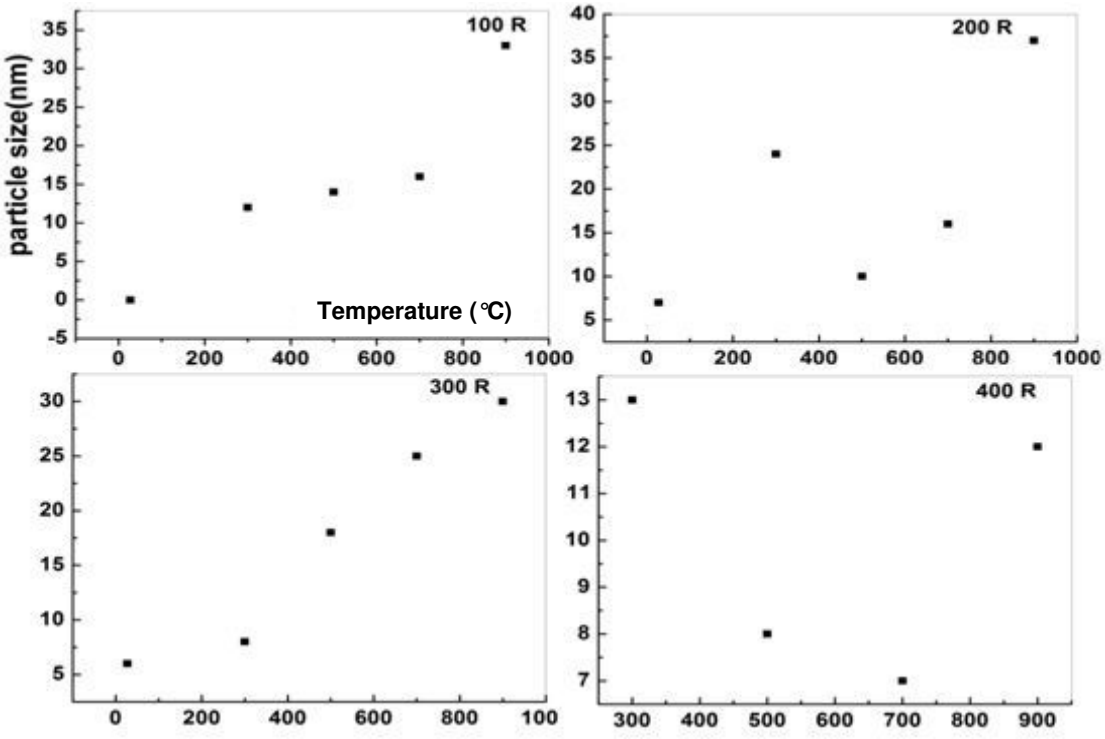

Figure 8. The size of TiO_2 particles were calculated by Scherer's equation, R= Rutile and numbers (from 100 to 400) is corresponding to Table 2.

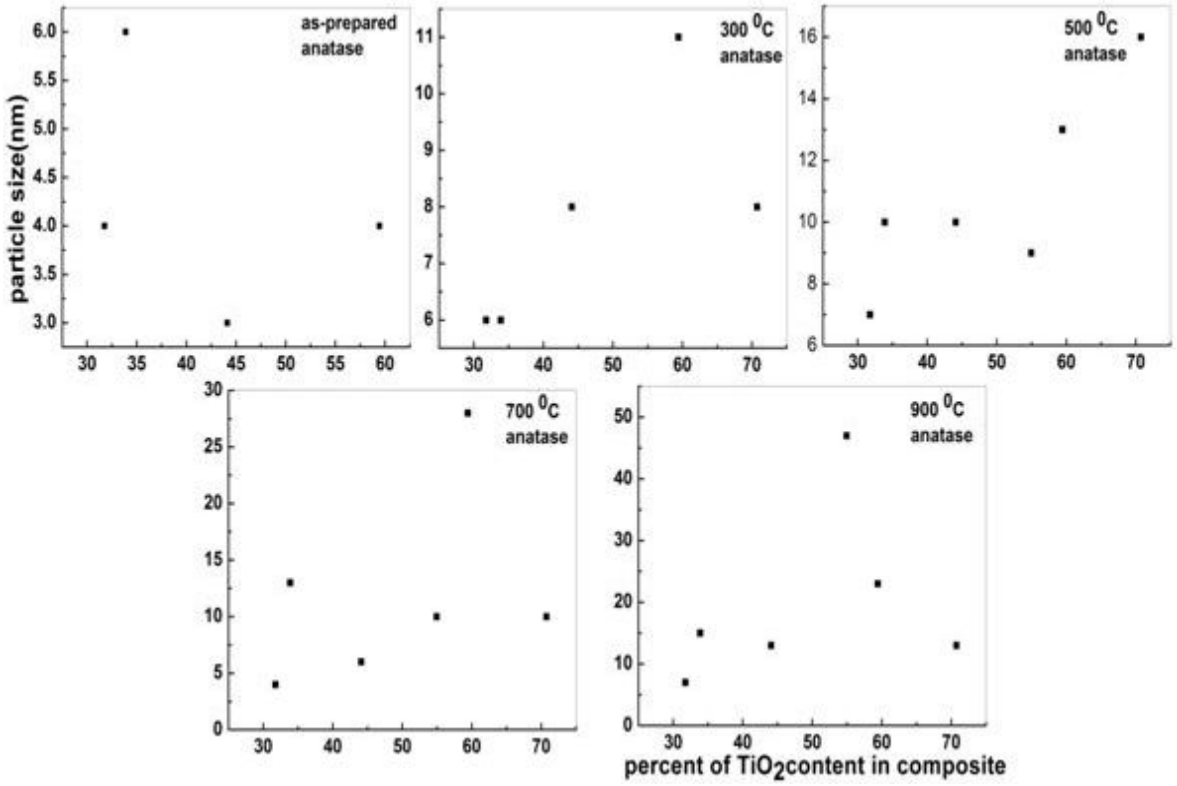

Figure 9. The size of TiO_2 (anatase phase) particles were calculated by Scherer's equation; TiO_2 percent in content is referred to in Table 2.

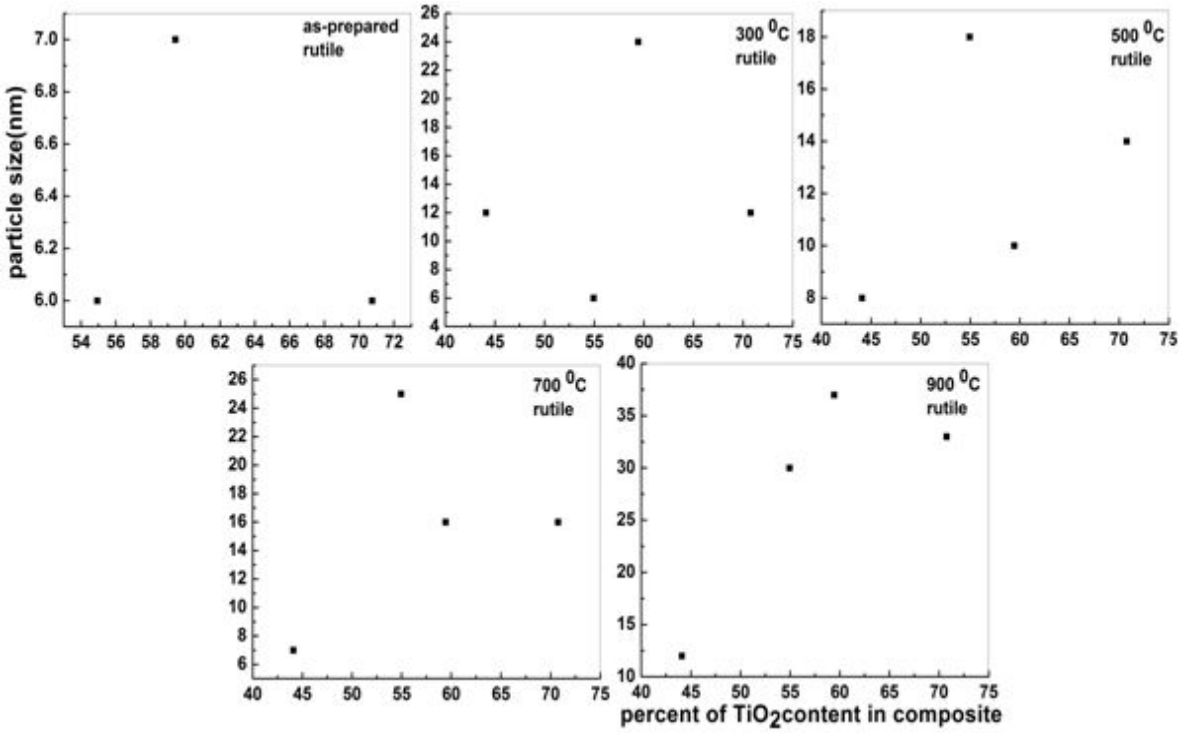

Figure 10. The size of TiO_2 (rutile phase) particles were calculated by Scherer's equation; TiO_2 percent in content is referred to in Table 2.

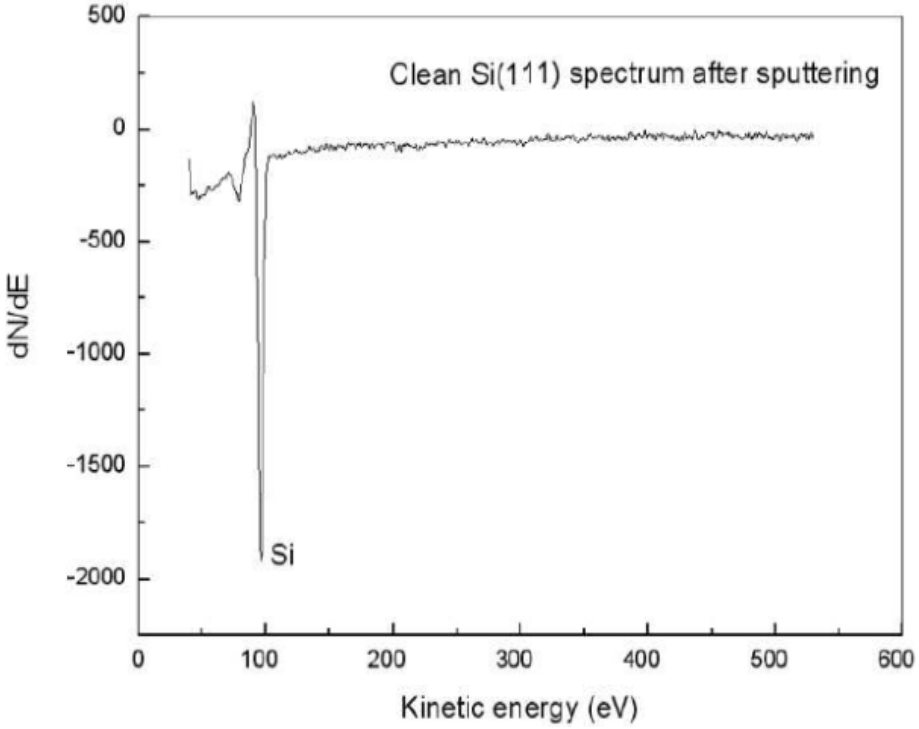

Figure 11. The silicon spectrum after sputtering. The energies of the peaks have been measured at the sharp minima. Clean Si has a major peak at 92 eV and small peaks at 75 eV, and 108 eV.

Table 3. The analysis of XRD patterns correspond to Table 2. The size of grain is derived by using Scherer's equation .The phase is also extracted from database of XRD patterns (A= Anatase, R= Rutile). The angle (2θ) corresponds to more insensitive peak relevant to anatase or rutile phase.

Temperature: 300°C				Temperature: As-Prepared			
Angle (2θ)	Phase	Size (nm)	Sample	Angle (2θ)	Phase	Size (nm)	Sample
	Anatase or Rotile				Anatase or Rotile		
25.4	A	8	100	27.4	R	6	100
27.6	R	12					
25.15	A	11	200	25.35	A	4	200
27.45	R	24		27.35	R	7	
27.5	R	8	300	27.35	R	6	300
25.5	A	8	400	25.2	A	3	400
27.6	R	12					
25.3	A	6	500	25.6	A	6	500
25.4	A	6	600	25.1	A	4	600

Temperature: 700°C				Temperature: 500°C			
Angle (2θ)	Phase	Size (nm)	Sample	Angle (2θ)	Phase	Size (nm)	Sample
	Anatase or Rotile				Anatase or Rotile		
25.4	A	10	100	25.5	A	16	100
27.5	R	16		27.6	R	14	
25.3	A	28	200	25.35	A	13	200
27.45	R	16		27.3	R	10	
25.45	A	10	300	25.25	A	9	300
27.5	R	25		27.5	R	18	
25.4	A	6	400	25.4	A	10	400
27.4	R	7		27.35	R	8	
25.35	A	13	500	25.3	A	10	500
25.3	A	4	600	25.35	A	7	600

Temperature: 900°C			
Angle (2θ)	Phase	Size (nm)	Sample
	Anatase or Rotile		
25.15	A	13	100
27.45	R	33	
25.3	A	23	200
27.4	R	37	
25.3	A	47	300
27.45	R	30	
25.25	A	13	400
27.35	R	12	
25.3	A	15	500
25.3	A	7	600

asymmetric stretching. The band near 950 cm^{-1} refers to Ti-O-Si asymmetric stretching. The peak near 798 cm^{-1} may be assigned to the O-Si-O vibration mode of SiO_2. The absorption band observed at about 950 $cm^{-1}$is associated with titanium in four-fold coordination with oxygen in the SiO_4^{-4} structure. Silicon oxide also gives a 950 cm^{-1} peak in the FT-IR spectrum, which is attributed to Si–OH band. Other titanium-associated absorptions occur in broad bands at 240 to 400 cm^{-1} and 650 to 730 cm^{-1}. These lie just below the host-silica absorptions at 450 and 798 cm^{-1}. In spite of the result of Zhao et al. [2004], this band does not still in the spectrum after

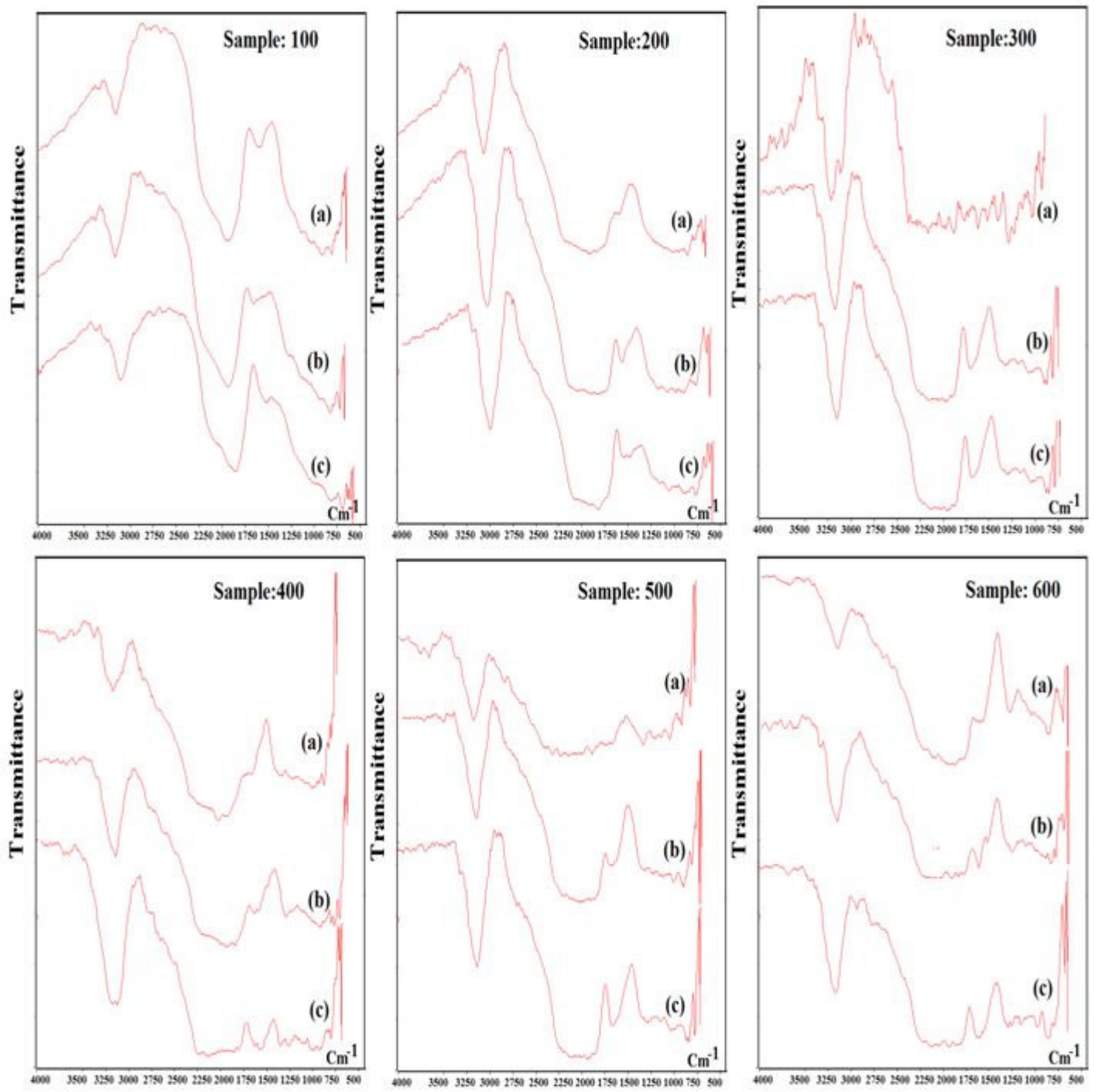

Figure 12. FT-IR spectra of mixed oxides according to Table 2 that a, b and c refer to 900, 500℃ and uncalcinated thermal treatment respectively.

heating treatment at 600 ˚C. We found that the intensity of the IR absorption peak is function of temperature and TiO_2 content. The prominent IR-active bands of pure silica are ascribed to TO modes of the SiO_4 network that have substantial motions of the light oxygen ions. These network modes involve vibrations of the bridging oxygen ions of corner-sharing SiO_4 tetrahedra. From this data [Bell et al., 1971; Kirk, 1988], we could conclude that

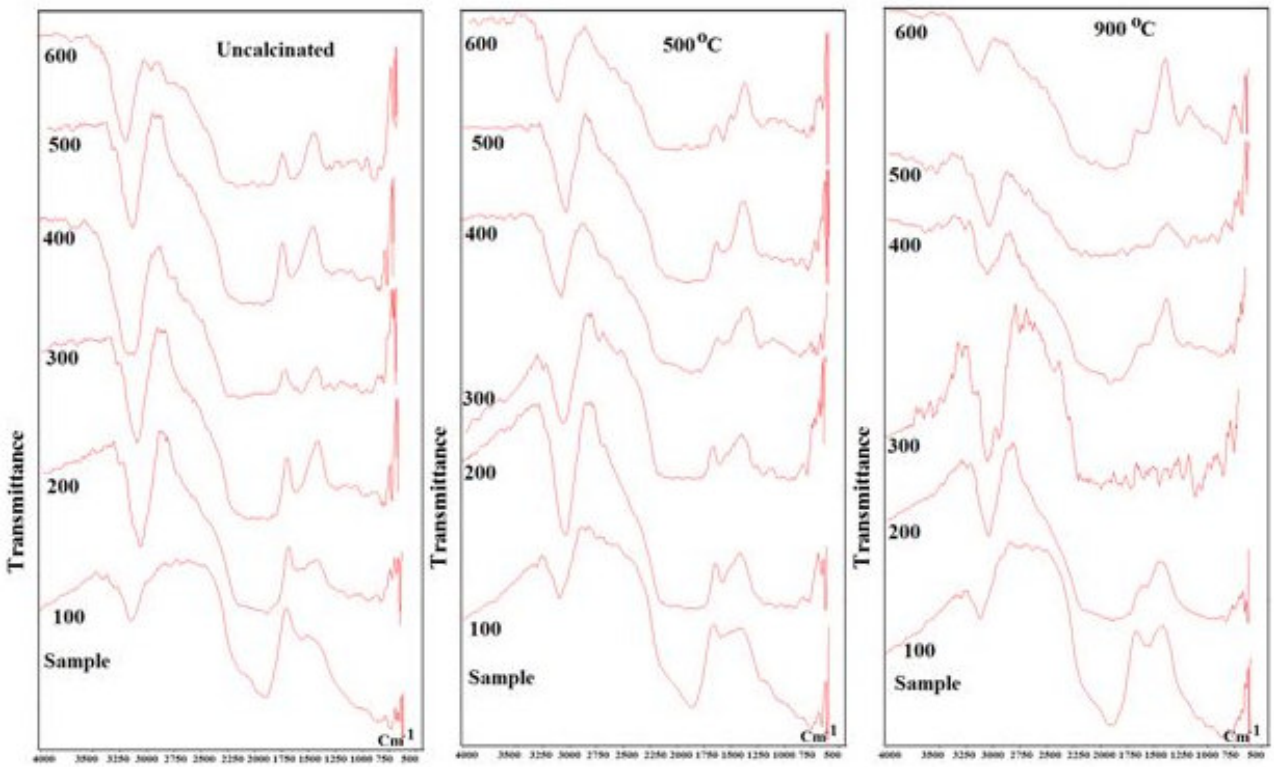

Figure 13. FT-IR spectra of the mixed oxide at the same calcination temperatures and different TiO_2 contents. The sample number labeled in figures. Are introduced in Table. 3.

titanium is in four coordination with oxygen in the SiO_4^{-4} structure, and each component in the materials is mixed on an atomic scale [Gribb and Banfield, 1997].

Conclusion

Thin amorphous TiO_2 film and binary metal oxide TiO_2-SiO_2 powder have been grown and synthesized, respectively. By increasing the temperature, the intensity of peaks in XRD patterns increase and crystallization are observable. Samples with TiO_2 content above 44% have rutile and anatase phases together whereas samples with lower content have only anatase phase. By increasing the TiO_2 content, rutile percent in mixture is explicit more than anatase and the particle size grow by increasing the calcination temperature.

The amorphous TiO_2 film can prevent leakage and tunneling current and Boron penetration through the ultra thin gate dielectric due to its high dielectric constant and small size of TiO_2 particles which resulting in production of more charge carriers and high surface area for opto electronic, photo catalysis and DRAM process. Thermal oxidation and nitridation methods have been proven to be accurate, reliable and to produce an extremely high quality film. Nonetheless there do remain other purposes for our work. Therefore, the largest fraction of nitrided silicon atoms is in the interface region, whereas the SiO_2/Si (100) structures contain more bulk oxide, for equivalent processing steps. To our knowledge, pure and amorphous nitride film can be grown on Si (100) substrate and be used for the future of CMIS (Complementary Metal-Insulator Semiconductor) devices.

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