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Surface, structural and electrical properties of $BaTiO_3$ films grown on *p*-Si substrates by low pressure metal organic chemical vapour deposition

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Metal organic chemical vapour deposition of $BaTiO_3$ using $Ba(tmhd)_2$, $Ti(OC_3H_7)_4$ and N_2O, where tmhd equals 2,2,6,6-tetramethyl-3,5-heptanedionate, via pyrolysis at relatively low temperatures ($\sim 370°C$) was performed in order to produce $BaTiO_3$ insulator gates. Scanning electron microscopy showed that the surfaces of the $BaTiO_3$ films had very smooth morphologies. Atomic force microscopy showed that the $BaTiO_3$ thin film was polycrystalline. X-ray diffraction results indicated that $BaTiO_3$ crystalline films grew on Si(1 0 0) with [1 1 0] orientation. High resolution transmission electron microscopy measurements showed that the $BaTiO_3$ films were polycrystalline, and an interfacial layer in the $BaTiO_3$/Si interface was formed. The stoichiometry and atomic structure of the $BaTiO_3$ films were investigated by Auger electron spectroscopy and transmission measurements, respectively. Room temperature capacitance–voltage measurements clearly revealed metal–insulator–semiconductor behaviour for samples with $BaTiO_3$ insulator gates, and interface state densities at the $BaTiO_3$/*p*-Si interface were approximately high, $10^{11}\ eV^{-1}\ cm^{-2}$, at the middle of the Si energy gap.

1. Introduction

The growth of epitaxial insulator films on Si has been particularly attractive in recent years due to their many promising applications, such as Si on insulator (SOI) structures and three-dimensional circuits [1–5]. Also, considerable interest in the growth of the insulator epitaxy exists because of its importance as a buffer layer prior to the growth of $YBa_2Cu_3O_{7-x}$ [6, 7]. Among various insulator films, barium titanate ($BaTiO_3$) is attractive due to its perovskite-type ferroelectric characteristics, such as its electron-optic properties, which have device applications [8, 9]. Some groups have reported the epitaxial growth of $BaTiO_3$ thin films using the deposition techniques of molecular beam epitaxy MBE [10], laser ablation [11] and metal organic chemical vapour deposition (MOCVD) [12–16]. Although the growth of $BaTiO_3$ epitaxial films was reported by Mckee *et al.* [10], to the authors' best knowledge, the only successful deposition of $BaTiO_3$ thin films with high quality interfaces have involved growth temperatures of at least 600 °C [10, 15, 16].

This paper reports the surface, structural and electrical properties of $BaTiO_3$ thin films deposited on *p*-Si (1 0 0) substrates by MOCVD at 370 °C. Scanning electron microscopy (SEM) and atomic

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force microscopy (AFM) measurements were performed in order to investigate the $BaTiO_3$ surface morphology, and X-ray diffraction (XRD) was used to characterize the structural properties of the $BaTiO_3$ films. Transmission electron microscopy (TEM) was performed to investigate the atomic structure of the $BaTiO_3$/Si, and transmission measurements were carried out to detect the bonding of the atoms. Furthermore, capacitance–voltage (C–V) measurements were performed to investigate the possibility of metal–insulator–semiconductor (MIS) behaviour for Au/$BaTiO_3$/p-Si diodes.

2. Experimental procedure

The carrier concentration and resistivity of the p-Si substrate with (1 0 0) orientation used in this experiment are approximately 1×10^{15} cm^{-3} and 10 Ωcm^{-1}, respectively. The β-diketonates complex of $Ba(tmhd)_2$ (where tmhd is 2,2,6,6-tetramethyl-3,5-heptanedionate), titanium iso-propoxide (TIP) and argon as the carrier gas were used. The temperatures of the oil baths for $Ba(tmhd)_2$ and TIP were maintained at 250 and 15 °C, respectively. The flow rates of the argon carrier gas for $Ba(tmhd)_2$ and TIP were 30 and 5 $sccm^3$, respectively. Heating tape was wrapped around the organometallic source vapour transport lines at 250 °C to prevent condensation from the source bath to the growth chamber. As soon as the chemical process was finished, Si substrates were mounted onto a molybdenum susceptor. N_2O gas was injected into the chamber at a system pressure of 133 Pa. The typical deposition time was carried out for 60 min and was followed by slow cooling to room temperature at a rate of 100 °C h^{-1} in an oxygen atmosphere to prevent strain-induced microcracks. In order to reduce the problem of vapour pressure reduction caused by surface melting of the barium precursor, the source was changed for every experimental run [13]. Detailed growth conditions are summarized in Table I.

3. Results and discussion

The as-grown $BaTiO_3$ film by MOCVD had mirror-like surfaces without any indication of pin holes, which was confirmed by Normarski optical microscopy. Although growth of the $BaTiO_3$ films had occurred in the temperature range 300–800 °C, the physical properties of the films grown at only 370 °C are reported because they had good surface morphology among several samples grown at relatively low temperatures. The SEM results of the $BaTiO_3$ films indicated a very smooth and dense surface morphology, as shown in Fig. 1. The AFM results of the $BaTiO_3$ films are shown in Fig. 2. The morphology of the films appeared rounded in shape, indicating the formation of polycrystalline grains. The average surface roughness of the $BaTiO_3$ films obtained from the AFM measurements is approximately 15 nm. The maximum different value between the peak and valley is about 30 nm. Ellipsometric measurements using the 632.8 nm line of He–Ne laser showed that the thickness of the $BaTiO_3$ films was approximately 200 nm, and that the refractive index was 2.2. Thus, the typical growth rate was about a few nanometres per second.

The stoichiometry of the grown $BaTiO_3$ films was investigated by AES measurements. The results of the AES measurements showed that the grown films consisted of barium, titanium, and oxygen. The ratios of the peak-to-peak intensities among the Ba_{KLL}, Ti_{KLL}, and O_{KLL} peaks of the $BaTiO_3$ films were similar to those obtained by Wills *et al.* [12]. There is no residual carbon detection and no significant change of stoichiometry throughout the thickness of the films, except near the interface. Silicon did not outdiffuse toward the films, resulting in a sharp interface. The detailed results of the Auger electron spectroscopy (AES) measurements were reported previously [14].

TABLE I $BaTiO_3$ growth conditions

Substrate	Si (1 0 0)
Substrate temperature, °C	300–800
Reactor pressure, Pa	133–266
Carrier gas	Argon
Deposition time, min	60 min
Flow rates, N_2O scm^3	70
TIP	5
$Ba(tmhd)_2$	30
Bath temperature, TIP °C	15
$Ba(tmhd)_2$	250

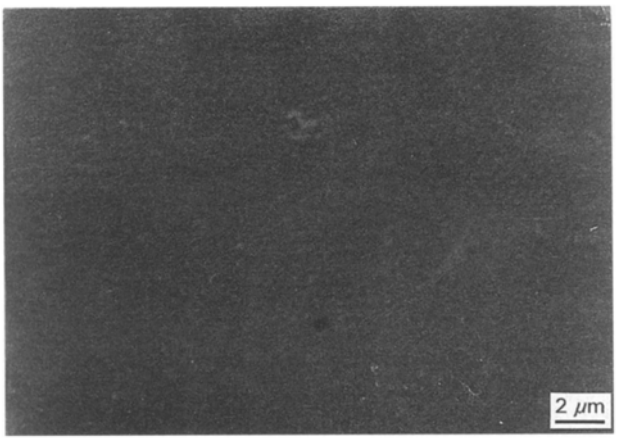

Figure 1 The result of scanning electron microscopy of the $BaTiO_3$ film on Si grown at 370 °C.

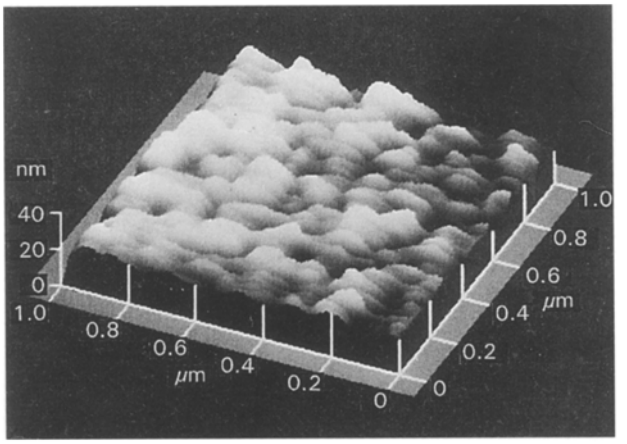

Figure 2 The results of atomic force microscopy of the $BaTiO_3$ film on Si grown at 370 °C.

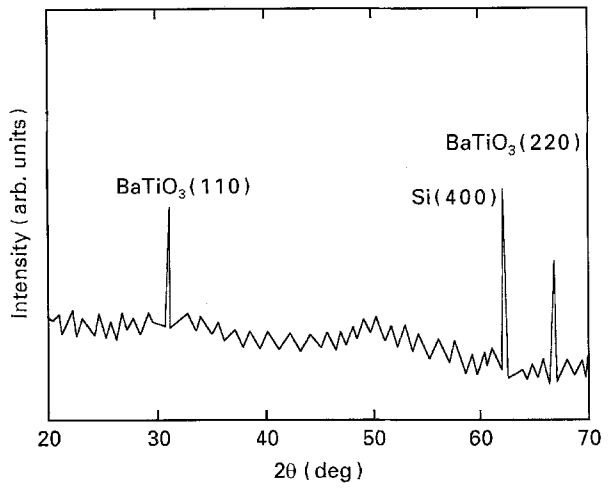

Figure 3 An X-ray diffraction pattern of the $BaTiO_3$ film on Si (1 0 0) grown at 370 °C.

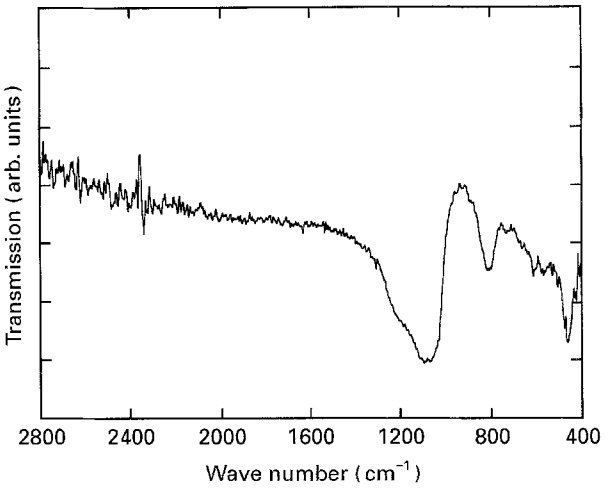

Figure 5 A transmission spectrum of the $BaTiO_3$/*p*-Si film on Si grown at 370 °C.

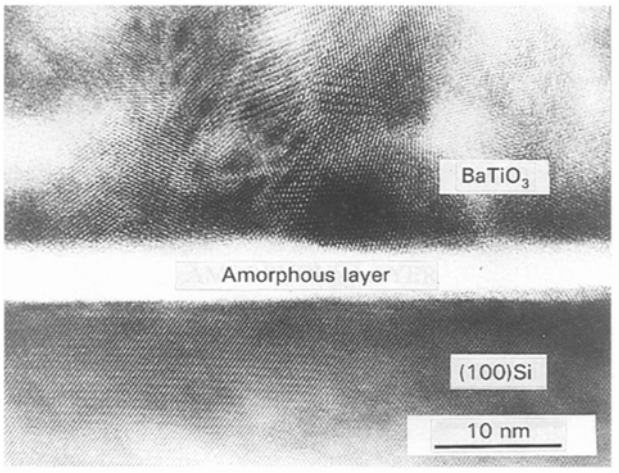

Figure 4 A high-resolution transmission electron microscopy image of the $BaTiO_3$/Si structure grown at 370 °C.

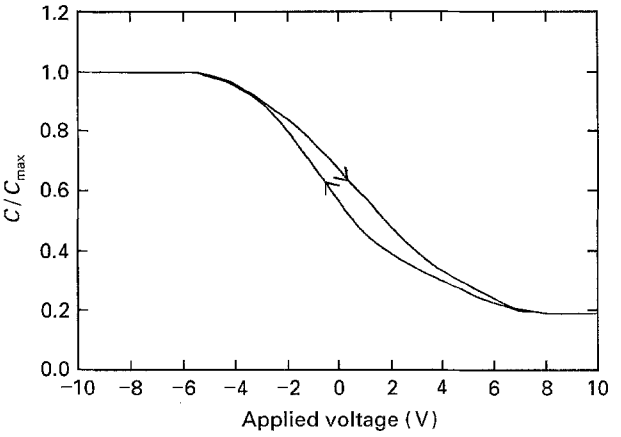

Figure 6 1-MHz capacitance–voltage curve of an Au/$BaTiO_3$/*p*-Si diode, where C_{max} = 128.88 pF; f = 1 MHz.

The results of the XRD measurements for a $BaTiO_3$ film deposited at 370 °C on Si (1 0 0) are shown in Fig. 3. The peaks show a highly orientated film growth, with the [1 1 0] $BaTiO_3$ direction normal to the Si(1 0 0). The lattice constant of a $BaTiO_3$ film determined from the XRD peaks corresponding to the (1 1 0) and (2 2 0) reflections is 0.4012 nm, and this value is in good agreement with that of cubic $BaTiO_3$ [12]. The full width at half maximum (FWHM) of the peak of $BaTiO_3$ (1 1 0) was approximately 0.23°. This value is a little smaller than that of 0.3° for the peak of epitaxially grown $BaTiO_3$ on $SrTiO_3$ [15].

A high resolution TEM image of the $BaTiO_3$/Si structure is shown in Fig. 4. The results of the TEM measurements indicate that an interfacial layer is formed in the $BaTiO_3$/Si interface and that the $BaTiO_3$ thin film is polycrystalline. The thickness of the interfacial layer at the $BaTiO_3$/Si interface is approximately 5 nm, and the chemical composition of the layer is TiO_2 [14]. Even though the main purpose was the growth of $BaTiO_3$ layers on Si substrates with high quality $BaTiO_3$/Si interfaces at relatively low temperature, the existence of an interfacial layer prior to the growth of $BaTiO_3$ might increase the interface state densities.

The spectral transmission of the film was recorded using a Hitachi 330 model visible and near infrared double-beam spectrophotometer. Fig. 5 shows a transmission spectrum of a $BaTiO_3$ thin film grown on a Si substrate at 370 °C. The transmittance exhibits sharp absorption edges at 1070, 810 and 540 cm^{-1}. The edge occurring at 1070 cm^{-1} is considered to be from Si–O bonding, and the edges occurring at 810 and 540 cm^{-1} are related to Ti–O bonding [17, 18].

In addition to the X-ray and TEM measurements, 1 MHz *C–V* measurements at room temperature were carried out to characterize the electrical properties of Au/$BaTiO_3$/*p*-Si. Ohmic contacts were fabricated by gold evaporation on the front side and by indium soldering on the back side of the samples. The behaviour in Fig. 6 is similar to that of *C–V* measurements of an ordinary prepared Al/SiO_2/Si diode [19]. The diameter of the top electrode used for *C–V* measurements is 0.5 mm, and the sweep rate used for recording the *C–V* curves is 10 mV s^{-1}. Since the thickness of the $BaTiO_3$ film determined from the ellipsometric measurements was 200 nm, the dielectric constant of the film grown at relatively low temperature was

obtained from the maximum capacitance of the structure under accumulation conditions [19]. The dielectric constant determined from the $C-V$ measurements was approximately 148. This value is lower than that of the $BaTiO_3$ film grown at higher temperature by MOCVD [13]. Instead of conductance–voltage measurements, the current-voltage ($I-V$) measurements were performed to investigate the possibility and leakage of an MIS diode using the $BaTiO_3$ layer as an insulator gate. The results of the $I-V$ characteristics for Au/$BaTiO_3$/p-Si at room temperature are similar to those of an Au/Si_3N_4/Si diode [19] and an Al/Ta_2O_3/SiO_2/Si capacitor [20]. There was no significant leakage problem within the reverse and forward applied voltages of 10 V. The interface state density at the $BaTiO_3$/Si interface determined by the Terman method [21] was approximately high $10^{11}\,eV\,cm^{-2}$ at the middle of the Si energy gap. Although this magnitude was somewhat higher than that of the high quality Al/SiO_2/Si structure, the value of the $BaTiO_3$/Si interface densities has sufficiently low application in MIS devices [19].

4. Conclusions

AFM, X-ray and TEM measurements showed that a $BaTiO_3$ polycrystalline film was grown by low pressure MOCVD at relatively low temperatures and that an interfacial layer was formed between $BaTiO_3$ and Si. The results of the $C-V$ measurements at room temperature clearly demonstrate MIS behaviour for the Au/$BaTiO_3$/p-Si substrates, and the interface state density determined by the Terman method was approximately high, $10^{11}\,eV\,cm^{-2}$, at the middle of the Si energy gap. These results suggest that a $BaTiO_3$ polycrystalline layer grown by MOCVD on p-Si has application for use in MIS diodes. Furthermore, $BaTiO_3$ insulator gates grown at low temperature give good motivation for fabrications of InP–MIS and InSb–MIS diodes.

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