—報　文—

タッチパネル用新規 In_2O_3 系透明導電膜材料の開発

秋　池　　　良[*1]
土　田　裕　也[*1]
原　　　浩　之[*1]
倉　持　豪　人[*1]

Novel In_2O_3 Based Transparent Conducting Oxide Material for Touch Screen

Ryo AKIIKE
Yuya TSUCHIDA
Hiroyuki HARA
Hideto KURAMOCHI

We would like to introduce our novel indium oxide based transparent conducting oxide (TCO). Novel TCO film showed lower resistivity by lower process temperature, 197 μΩ·cm at 150℃, 217 μΩ·cm at 100℃ respectively. It can be applied to flexible touch screen (TS) favorably. This development accelerates the investigation of flexible device, which enable to access to internet easily. Our development will contribute the saving energy on the point of reduce a process temperature.

1. INTRODUCTION

In_2O_3 based transparent conductive oxide film has been widely applied to electronic devices, flat panel display (FPD), some kinds of photovoltaic devices, and touch screens. Tin doped In_2O_3 (ITO) is well known as most acceptable TCO with high conductivity, transparency and stability. ITO exhibits a low resistivity when it deposited on glass substrates with over 200 ℃ process temperature [1] [2].

Recently, flexible devices have become attractive from the viewpoint of thinner, light weight. Conventional flexible device is manufactured on polymer material substrate. Hence, TCO is deposited on flexible polymer substrate instead of glass. Therefore, process temperature has to be suppressed less than glass transition temperature.

Focused on a flexible touch screen, the requirement of resistivity is less than 250 μΩ·cm by less than 150℃ (the average of process temperature of PET, PEN = 130 ℃ ~ 170 ℃) [3]. The film thickness is restricted under 50nm not to confirm visually. These properties are hard to achieve by ITO.

In this work, we successfully developed novel In_2O_3 based TCO fulfilled the above-mentioned requirement. We would like to introduce novel TCO film properties and their sputtering target.

2. EXPERIMENTAL

2.1 Preparation of sintered body and sputtering target

Our novel TCO (named USR) consists of In_2O_3 and

＊1　アドバンストマテリアル研究所

the other additives. USR sintered body was prepared by simply resistance heating method reported elsewhere [4][5]. Commercial powder of In_2O_3 and the other additives (the purity was over 99.9%) were used as starting materials. After the sintering, the obtained sintered body has more than 99% relative density. A USR sputtering target was fabricated from this sintered body by grinding and cutting.

2.2 Deposition of USR film

The USR film was deposited on a substrate by DC magnetron sputtering. The sputtering conditions are shown in **Table.1**.

After deposition, the film samples were annealed at 150℃ in a lamp anneal furnace for 60 min with heating rate of 50℃ /min under ambient atmosphere.

The measurement of film properties was investigated by following methods. Electrical properties were measured by van der Paw's method to analyze between career density and mobility. Transmission and reflection spectra of visible wavelength region were measured by spectrometer. The micro crystal structure of film was observed by electron back scattering diffraction (EBSD) method.

Table. 1 Sputtering conditions

Parameter	Conditions
Back ground presure (Pa)	8.5×10^{-5}
Sputtering gas	Ar
O_2 partial pressure (%)	0.5
Power (W/cm^2)	4.5
Pressure (Pa)	0.7
Temperature	Room temperature (without any heating)
Film thickness (nm)	30

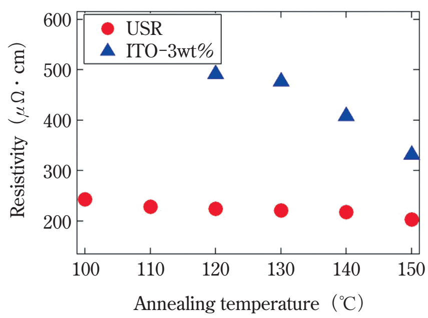

Fig. 1 Temperature dependence of electrical resistivity of USR film (annealing time : 60min)

3. RESULTS AND DISCUSSION

3.1 Electrical property

Fig.1 shows temperature dependence of electrical resistivity of USR and ITO (In_2O_3: SnO_2 = 97: 3 wt%). USR Film resistivity of 217μΩ·cm can be achieved even at 100 ℃ . Notably, USR film showed almost same resistivity between 100 ℃ and 150 ℃ . This result indicates annealing temperature can be suppressed at 100 ℃ . Therefore, many kinds of polymer materials can be used as USR's substrate. USR film is considered as suitable TCO materials for flexible device.

The detail of an electrical property of USR film after 150℃ post annealing showed 197μΩ·cm (**Table.2**). This resistivity is significant lower value compared with ITO. Especially, a career mobility of USR exhibit 1.4 times higher value than that of ITO. This relation was sustained when the mass of Sn was adjust to that of USR'additives (data is not shown).

For a better understanding the electrical property of USR film, EBSD measurement was carried out to analyze the micro crystal structure of polycrystalline films. **Fig.2** shows EBSD image of USR and ITO. Although almost all region of polycrystalline films consist of typical cubic (bixbyite) structure, further observation revealed that trigonal (corundum) type In_2O_3 exists at grain boundary (Both crystal structures can be seen in **Fig.3**). According to EBSD quantitative analysis of corundum phase, the sum of corundum area of USR is about 5 times larger than that of ITO.

Corundum phase In_2O_3 is known as In_2O_3 polymorph transition from bixbyite phase at high pressure and high temperature [6][7]. Karazhanov et al. reported first principle calculation and band structure analysis of bixbyite and corundum phase In_2O_3. Their analysis indicated that calculated effective masses for bixbyite phase are considerable larger than those for corundum

Table. 2 Electrical properties of USR film (annealing temperature : 150℃)

Parameter	USR	ITO (SnO_2:3wt%)
Resistivity (μΩ・cm)	197	331
Sheet resistance (Ω/□)	64.0	108
Mobility (cm^2/Vs)	51.0	37.1
Career density ($-/cm^3$)	6.04×10^{20}	5.7×10^{20}
Film thickness (nm)	31.2	30.6

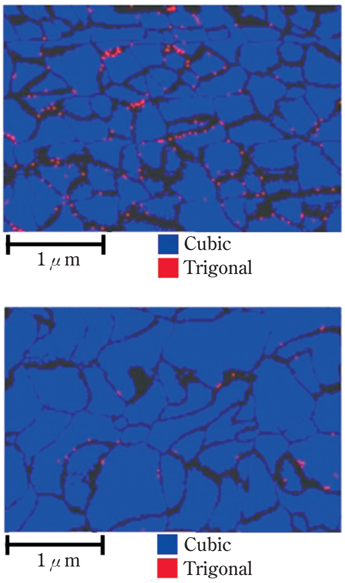

Fig. 2　EBSD images of USR film (top) and ITO film (bottom) after annealing (annealing temperature: 150 ℃)

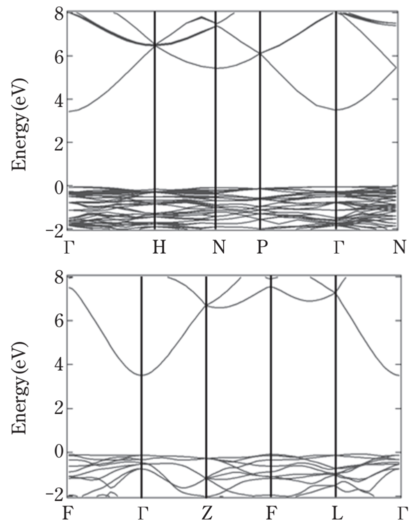

Fig. 4　Band structure of top: cubic (bixbyite) In_2O_3 and bottom: trigonal (corundum) In_2O_3

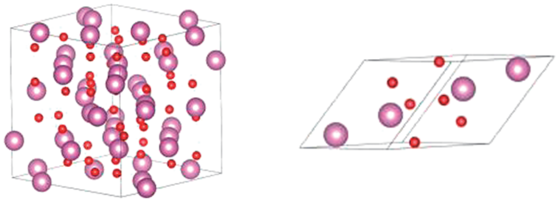

Fig. 3　Crystal structure of left: cubic (bixbyite: space group =206) In_2O_3 and right: trigonal (corundum: space group=167) In_2O_3
In atoms are violet, O atoms are red

phase [8]. Band structures of bixbyite and corundum In_2O_3 are shown in **Fig.4**. The calculations were performed with VASP package[9]. The cut-off energy was set to 500nm. Structural optimization has been performed with PBEGGA[10] on a G centered 9 × 9 × 9 k grid for corundum phase and 3 × 3 × 3 k grid for bixbyite phase respectively. After optimization, band structure was calculated with hybrid function HSE06[11] with AEXX =0.38 and AGGAX=0.62. Fermi level was set to zero. Our results support ref [8]. The conducting band minimum of corundum phase is more dispersive than that of bixbyite phase. The smallest effective masses were calculated as 0.12 for corundum phase(Γ → Z) and 0.18 for bixbyite phase(Γ → N) respectively.

These results mean a career mobility of corundum phase is expected to be higher than that of bixbyite phase. Hence corundum phase of USR film may contribute the enhancement of career mobility.

3.2　Optical property

Optical property of USR film was also studied. TCO for touch screen is required high transparency at visible wavelength region. **Fig.5** shows transmission spectra of USR and ITO deposited on glass substrate. Dotted line is the spectrum of glass substrate. Although transparency of USR film was almost same as ITO, There is a difference around 300 ～ 400nm region. USR film showed a slightly higher transmittance even in 30nm thickness. This region is considered as band absorption. Thus it is assumed this difference is caused by Burstein-Moss effect. As considered **Table.2**, a career density supports this assumption.

Fig.6 shows reflectance spectra of USR and ITO respectively. Both of them showed similar spectra at visible wavelength. Therefore, similar anti-reflective coating layer can be applied to fabricate a device.

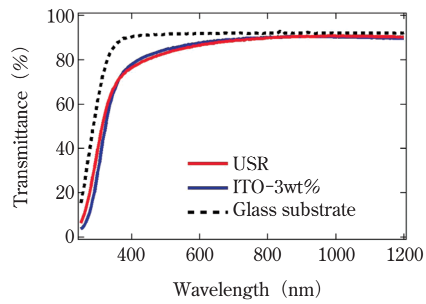

Fig. 5　Transmission spectra of USR film and ITO after annealing (annealing temperature : 150℃)

3.3 Stability

For practical application of USR film, the stability of electrical property was investigated. The accelerated degradation test with conditions of 85℃, 85% relative humidity for 1000 hour was carried out. The result is seen in **Fig.7**. Y axis means the relative ratio of electrical resistivity between before and after degradation. The relative ratio after 1000 hour was almost same value between USR and ITO. This result indicates USR film has good enough stability as ITO film has so that ITO can be substituted for USR.

4. Conclusion

In summary, we developed novel In_2O_3 based TCO "USR". The sintered body of USR can be synthesized ordinary sintering scheme and fabricated a sputtering target. The film deposition was carried out room temperature and then annealed under ambient atmosphere. A high annealing temperature was not necessary, 197 $\mu\Omega\cdot$cm can be achieved at 150℃ and 217 $\mu\Omega\cdot$cm can be achieved at 100℃ respectively. USR film has large number of corundum phase In_2O_3 at crystal grain boundary compared with ITO film. These crystals were considered that they contribute the improvement of electrical property. Optical property and stability was almost same as ITO. These aspects allow us to treat them as if it is ITO.

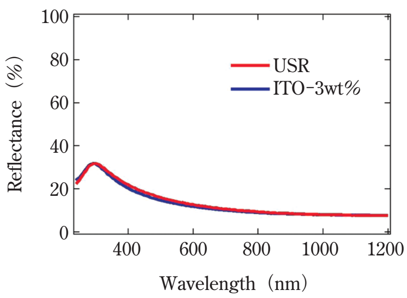

Fig. 6 Reflectance spectra of USR film and ITO after annealing (annealing temperature : 150℃)

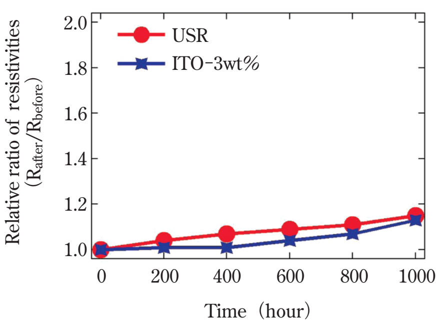

Fig. 7 Accelerated degradation test of the electrical property of USR film.

REFERENCES

[1] M. Huang, Z. Hameiri, A. G. Aberle, Vacuum., 121, 187 (2015)

[2] T. Karasawa, Y. Miyata, Thin Solid Films., 223, 135 (1993)

[3] T. Hayashi, "TOUCH PANEL SAIZENSEN 2013-3014", 105

[4] M. Muraoka, M. Suzuki, Y. Sawada, J. Mater. Sci., 33, 5621 (1998)

[5] M. Suzuki, M. Muraoka, Y. Sawada, J. Matsushita, Mater. Sci. Eng. B., 54, 46 (1998)

[6] A. Gurlo, P. Kroll, R. Riedel, Chem. Eur. J., 14, 3304 (2008)

[7] B. García-Domene, J. A. Sans, F. J. Manjón, S. V. Ovsyannikov, L. S. Dubrovinsky, D. Martinez-Garcia, O. Gomis, D. Errandonea, H. Moutaabbid, Y. Le Godec, H. M. Ortiz, A. Muñoz, P. Rodríguez-Hernández, C. Popescu, J. Phys. Chem. C., 119, 29076 (2015)

[8] S. Zh. Karazhanov, P. Ravindran, P. Vajeeston, A. Ulyashin, T. G. Finstad, and H. Fjellvag, Phys. Rev. B., 76, 7, 075129 (2007)

[9] G. Kresse and J. Furthmüller, Phys. Rev. B., 54, 11 169, (1996)

[10] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett., 77, 3865 (1996)

[11] A. V. Krukau , O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, J. Chem. Phys., 125, 224106 (2006)