Stabilization of Characteristics by Hydrogen Plasma Treatment for Top-gate Thin-film Transistor Using High-mobility Oxide Semiconductor, a-IGZTO

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Abstract

Top-gate thin film transistors (TFTs) using a high mobility oxide semiconductor, amorphous In-Ga-Zn-Sn-O (a-IGZTO), are attracting much attention in the field of flat panel displays. Here, the effectiveness of hydrogen plasma treatment for the formation process of low electrical resistance source/drain has been clarified. The hydrogen plasma treatment has reduced the sheet resistance of an a-IGZTO film, and this low resistance state has demonstrated high stability under heat treatment. An X-ray photoelectron spectroscopy confirmed the OH group's existence after argon plasma irradiation, suggesting that a-IGZTO has been physically sputtered. Meanwhile, it has been shown that hydrogen plasma irradiation causes the a-IGZTO to be reduced by hydrogen radicals, the reduction reaction producing metallic components. This reduction reaction is considered to have made the top-gate type TFT treated by hydrogen plasma more stable under heat treatment.

Introduction

New technologies, such as big data, AI, IoT, and automated driving, enrich our society more and more. Electronic devices support this digital society, and one of the essential elements is transistors, which have a current control function. Before transistors, vacuum tubes were used in electronic devices, but they could not be made smaller. The invention of transistors paved the way for miniaturization and high performance, and today we live in a society that uses electronic devices in all aspects of life. Silicon is often used as the semiconductor material for transistors, and the history of electronic devices can be described as a history of the evolution of transistors based on silicon. In the field of displays, one of the electronic devices, thin film transistors (hereinafter called "TFTs") using amorphous silicon (hereinafter called "a-Si"), which can be manufactured in large areas at low costs, are widely used. In recent years, oxide materials that exhibit semiconductor characteristics (hereinafter referred to as "oxide semiconductors") have been proposed as new materials, other than silicon, to meet the increasing demand for higher-performance TFTs. Oxide semiconductors are materials that can achieve 20 times higher mobility than a-Si TFTs, while having the same capability as a-Si to form a thin film over a large area. For example, amorphous In-Ga-Zn-O (a-IGZO)[1), 2)] and amorphous In-Ga-Zn-Sn-O (a-IGZTO)[3), 4)] with higher mobility are mass-produced as semiconductor materials for LCDs used in TVs, tablets, and notebook PCs. Recently, their application to Organic Light Emitting Diodes (OLEDs) has been increasing, and further expansion into the semiconductor field, such as memory, is also being considered. Kobe Steel has been developing oxide semiconductor materials and TFT processes in response to this market expansion.

In OLEDs, which are current-driven, the parasitic capacitance of the TFT must be reduced to stabilize the characteristics. In order to reduce parasitic capacitance, it is essential to change the TFT structure from the conventional bottom-gate structure to a top-gate (also called planar) structure.[5)] One of the most significant differences between the top-gate and bottom-gate structures is in making the oxide semiconductor layer conductive (semiconductor-conductor conversion process). In the top-gate structure, the resistance of the oxide semiconductor film can be selectively reduced by masking the gate electrode and applying semiconductor-conductor conversion. Using this low-resistance region as a source/drain region (hereinafter referred to as an "S/D region") advantageously eliminates the overlap between the gate electrode and the S/D region, thereby reducing parasitic capacitance. However, to a function as a TFT, it is necessary to create regions with two types of characteristics, semiconductor and conductor, within a single activation layer (e.g., a-IGZTO). Several methods have been proposed to form the S/D region, including plasma treatment,[6)-9)] reaction with aluminum,[10), 11)] ion implantation,[12), 13)] and laser exposure.[14)] Among these, hydrogen plasma exposure is expected to cause less physical damage to oxide semiconductors because of the lighter mass of hydrogen. In addition, oxide semiconductors tend to be converted easily into conductors in the presence of hydrogen,[15)] and this tendency is more pronounced in high mobility materials; so hydrogen plasma exposure is expected to entail low resistance. In addition, it is known that oxide semiconductors generally have increased conduction carriers due to oxygen deficiency. However, heat treatment can adjust the number of carriers to an appropriate level and improve TFT characteristics.[16] Hence, a semiconductor-conductor conversion process that is stable against heat treatment during fabrication is required.

Hence, Kobe Steel has developed a fabrication process for the high mobility oxide semiconductor a-IGZTO, using hydrogen plasma with a wide process window for heat treatment. This paper shows that the transfer characteristics of a top-gate TFT that has undergone hydrogen plasma treatment include excellent heat resistance. Also reported are the study's results using X-ray Photoelectron Spectroscopy (XPS) on the source-drain formation mechanism by hydrogen plasma treatment.

1. Experimental method

In order to evaluate the sheet resistance and chemical bonding state of an a-IGZTO film, 40 nm thick films of a-IGZTO were deposited by DC magnetron sputtering on glass substrates under gas pressure of 0.13 Pa and an $O_2/(Ar+O_2)$ flow ratio of 4%. The deposited a-IGZTO films were heat treated at 350℃ for 1 h in air and exposed to argon or hydrogen plasma. For plasma exposure, parallel-plate plasma apparatuses with different RF power were used. Sheet resistance was measured for each plasma-exposed film by a four-point probe method before the XPS measurement.

Fig. 1 shows the cross-sectional structure corresponding to each fabrication step of a-IGZTO-TFT used to evaluate transfer characteristics and the test element group (TEG) to evaluate sheet resistance change during the fabrication process. A buffer layer of SiO_2 was formed on a glass substrate by plasma-enhanced chemical vapor deposition (hereafter referred to as PE-CVD.) Then a-IGZTO was deposited to form a film 40 nm thick by DC magnetron sputtering with the substrate temperature set to room temperature, followed by patterning by wet etching. Subsequently, after heat treatment at 350℃ for 1 h in the atmosphere, a SiO_2 gate insulator (hereinafter referred to as "GI") films of 150 nm were deposited by PE-CVD

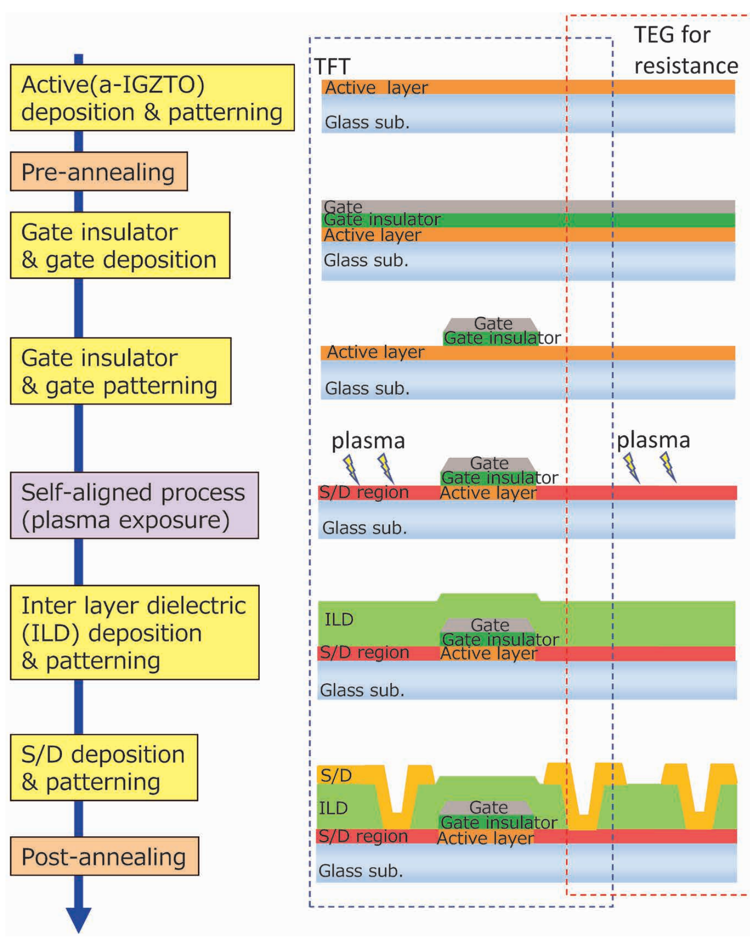

Fig. 1 Fabrication flow and cross-sectional schematics of top-gate TFT and test element group (TEG) for resistance

at temperatures from 250 to 300℃ using a SiH_4/N_2O gas mixture. Next, the Mo gate electrode was deposited by DC magnetron sputtering, the gate electrode was patterned by wet-etching, and the gate insulator film was patterned by reactive ion etching (RIE). Furthermore, the S/D region was formed by exposing the oxide semiconductor surface to argon or hydrogen plasma, using the gate electrode as a mask. Then, an SiO_2 protective film was formed by PECVD, and contact holes were formed by dry etching. This was followed by forming S/D electrodes of Mo alloy by DC magnetron sputtering. Transfer characteristics were measured with a semiconductor parameter analyzer. The test element group (TEG) for resistance, which underwent the same process as the TFT, was also measured to evaluate the change in electrical resistance of the S/D region.

2. Experimental results and discussions

2.1 Stability of TFT transfer characteristics under heat treatment

Fig. 2 shows the dependence of sheet resistance on the plasma exposure time when argon plasma treatment and hydrogen plasma treatment are applied to an a-IGZTO thin film deposited on a glass substrate. The sheet resistance of the a-IGZTO thin film after film deposition and heat treatment (pre-anneal) is approximately 10^4 kΩ/□, and the sheet resistance has decreased significantly in both of the plasma treatments. Even an exposure time as short as 15 s is considered sufficient.

Fig. 3 shows the plasma exposure time dependence of TFT transfer characteristics using the hydrogen plasma exposure process. As confirmed by the sheet resistance measurement, excellent TFT transfer characteristics were obtained even with a short plasma exposure time. In addition, a slight shift of the threshold voltage to the negative voltage direction is observed as the plasma exposure time increases.

Fig. 4 (a) shows the stability of drain current against a heat treatment, post-annealing, of TFTs with argon plasma and hydrogen plasma exposure. At post-annealing temperatures below 200℃, there is no decrease in drain current for either argon plasma-exposed or hydrogen plasma-exposed TFTs. However, for the argon plasma-exposed TFT, the drain current decreased rapidly with the increasing post-annealing temperature above 200℃. On the

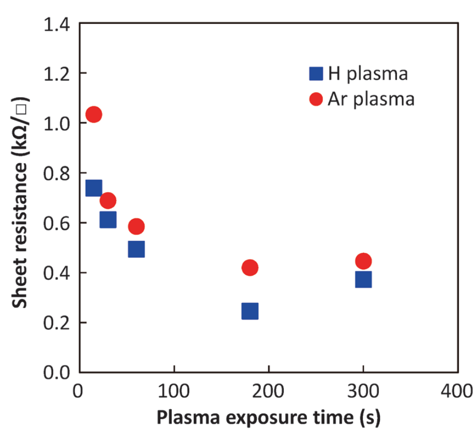

Fig. 2 Dependence on plasma exposure time of sheet resistance on oxide semiconductor (a-IGZTO)

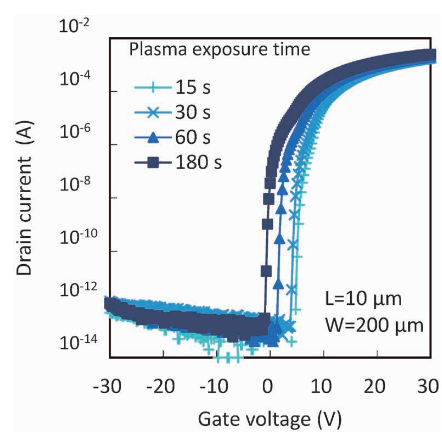

Fig. 3 Dependence of hydrogen plasma exposure time of Id-Vg curve of top-gate TFT

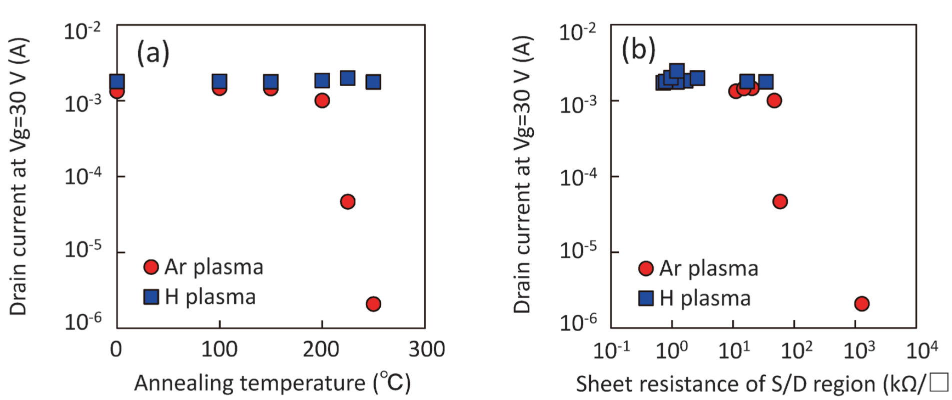

Fig. 4 (a) Dependence on annealing temperature of drain current, (b) Relation of drain current vs. sheet resistance on S/D region of a-IGZTO other hand, the TFT exposed to hydrogen plasma shows no decrease in the drain current at least up to 250℃. In order to discuss the change in drain current due to the difference in the plasma exposure methods, the relationship between drain current and sheet resistance in the S/D region is shown in Fig. 4(b). The sheet resistance in the S/D region was measured for TFT devices on the same substrate (devices fabricated in the same process), as shown in Fig. 1. When the sheet resistance in the S/D region exceeds approximately 50 kΩ, there is a sharp drop in the drain current. Since this value of 50 kΩ corresponds to the conductivity required for 1 mA flow in Kobe Steel's TFT structure, it is considered that the resistance in the S/D region increased due to the heat treatment, becoming a resistance component and causing a rapid decrease in drain current.

2.2 Consideration of formation mechanism of S/D region, using XPS analysis

Oxidation of the constituent elements of an a-IGZTO is suspected to be the cause of the increased resistance of the oxide semiconductor. In order to capture the changes in chemical state such as oxidation-reduction, the changes in the bonding state of oxide semiconductors exposed to hydrogen plasma and argon plasma, respectively, were examined by XPS analysis. The effect of the TFT fabrication process was evaluated. The heat-treated a-IGZTOs were exposed to a CHF_3/Ar mixed gas plasma that simulates dry etching of a gate-insulating film by the RIE process (hereinafter referred to as RIE plasma.) Then, for a chemical derivatization, they were exposed to argon plasma and hydrogen plasma, respectively, before being subjected to XPS analysis. Among the a-IGZTO constituent elements, focus was placed on In as the carrier source. A comparison was made on the effect of plasma treatment on In 3 $d_{5/2}$ peak, which has a relatively significant difference in chemical shifts among metals, oxides, and hydroxides (**Fig. 5**). The In 3 $d_{5/2}$ peak was separated using the peaks at 443.73 eV corresponding to metallic In, 444.65 eV corresponding to In_2O_3, and 445.13 eV corresponding to $In(OH)_3$. Each peak's full width at half maximum (FWHM) was set to 1.8 eV. The FWHM was assumed to remain unchanged due to the process. Before the plasma treatment, the peak at 444.65 eV corresponding to In_2O_3 is dominant (Fig. 5(a)). In contrast, a peak at 445.13 eV corresponding to $In(OH)_3$ hydroxide grows in a (CHF_3/Ar) mixed gas simulating the RIE plasma process for gate insulating film (Fig. 5(b)). In the case of RIE plasma, fluorine radicals, hydrogen radicals, and argon ions exist in the plasma. Therefore, the reaction of the oxide semiconductor with fluorine radicals (or C-Fx), the reaction with hydrogen radicals, and the sputtering effect of argon ions are considered to act in a combined manner. Next, the effect of plasma

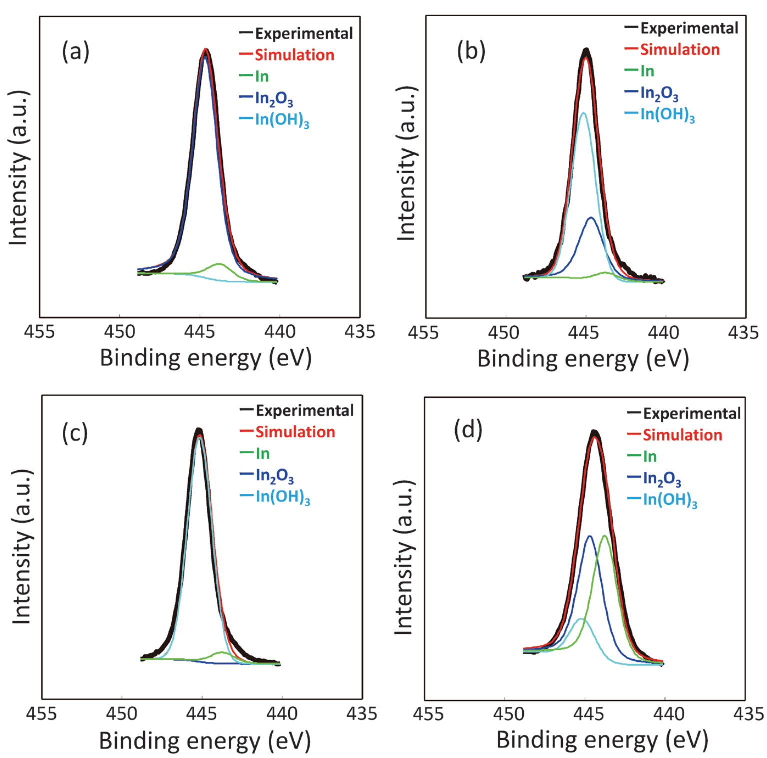

Fig. 5 In 3$d_{5/2}$ peaks of XPS spectra on the a-IGZTO thin film surfaces, (a) no plasma exposure, (b)after RIE, (c) RIE and argon plasma, and (d) RIE and hydrogen plasma exposure

exposure was confirmed. As shown in Fig. 5 (c), the peak corresponding to $In(OH)_3$ increases after argon plasma exposure. On the other hand, as shown in Fig. 5(d), after hydrogen plasma exposure, the In 3 $d_{5/2}$ peak significantly shifts to the low energy side, the ratio of the hydroxide peak decreases, and the peak indicating metallic bonding appears. This result suggests the reduction of In by hydrogen plasma exposure. It should be noted that similar results have been obtained when the RIE plasma process is omitted, indicating that there is little influence of the RIE plasma process and the semiconductor-conductor conversion process is dominant.

On the basis of these results, the possible mechanisms of the effects of argon plasma exposure and hydrogen plasma exposure on a-IGZTO are shown in **Fig. 6**. The effect of argon plasma treatment is presumed to be physical sputtering of the surface by argon ions. The surface is sputtered, and the deficiency of oxygen, serving as a carrier source, is considered to cause low resistance.[8] It should be noted, however, that because of the large mass of argon ions, oxygen atoms, and all atoms constituting a-IGZTO (In, Ga, Zn, Sn, and O) are sputtered to form dangling bonds. It is assumed that the topmost surface of a-IGZTO is modified with OH groups by subsequent exposure to moisture in the atmosphere, as observed by XPS. On the other hand, since the mass of hydrogen atoms is much smaller than that of argon atoms, the hydrogen plasma treatment should bring on a much smaller physical sputtering effect on the a-IGZTO surface. In hydrogen plasma, hydrogen cation (proton) generated by the ionization of hydrogen removes O or OH groups from the surface of the a-IGZTO. In other words, the reduction of In-O bonding and the formation of metallic bonding are considered to have increased the number of carriers and decreased the electrical resistance in the S/D region. Thus, although the same resistance reduction phenomenon occurs on a-IGZTO, the argon plasma treatment and hydrogen plasma treatment have different resistance reduction mechanisms, which is considered to have caused the difference in the effect on the TFT characteristics. Thermal desorption spectrometry (TDS) of a-IGZTO shows that the desorption of the OH group begins at around 100℃, and desorption of In is observed at 400℃ and above. Therefore, the In-In bond is presumed to be more stable than the In-OH bond. As shown in Fig. 3, the threshold voltage of the TFT tends to shift in the negative voltage direction as the hydrogen plasma exposure time is increased. The fact that the TFT characteristics were affected even though the channel was not exposed to the plasma suggests that the proton from the hydrogen plasma penetrated the a-IGZTO film. Based on the above results, hydrogen plasma treatment produces a more stable metal component on the a-IGZTO surface than argon plasma treatment, making the surface less susceptible to oxidation by subsequent heat treatment. The effect of the oxidation on the material's surface extends to the interior, and the low resistance state of the interior is maintained even when the surface is oxidized, indicating high heat resistance, as shown in Fig. 4.

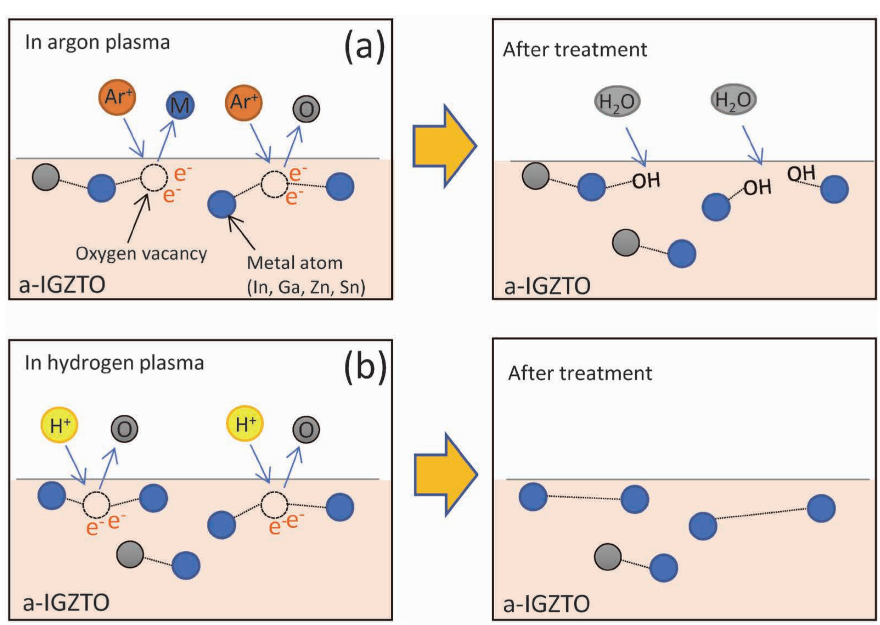

Fig. 6 Schematic representation of a possible mechanism to explain the difference between the (a) argon and (b) hydrogen plasma exposure

Conclusions

A high-mobility a-IGZTO TFT with a top-gate structure for OLEDs has been shown to have a wide process window for heat treatment when fabricated using hydrogen plasma. In the semiconductor-conductor conversion using hydrogen plasma, XPS analysis has shown that the metal component increases due to the reduction of oxide semiconductors by a proton. As a result, it has been found that the insulator-conductor conversion state of a-IGZTO is stabilized, and the increase in electrical resistance due to heat treatment is suppressed.

This paper has reported on the latest materials and process influences on oxide semiconductors for displays. In the field of electronic devices such as semiconductor memories, the application of oxide semiconductors has begun to be investigated for higher performance, and the evaluation results for semiconductor memory using Kobe Steel's a-IGZTO have been reported.[17)] The knowledge of process design guidelines based on material development and analytical techniques obtained in the development of oxide semiconductors can also be applied in this field. Kobe Steel will strive to contribute to the further expansion of the use of oxide semiconductors.

References

1) K. Takechi et al. J. Appl. Phys. 1998, Vol.84, pp.3993-3999.
2) K. Nomura et al. Nature. 2004, Vol.488, p.432.
3) M. Ochi et al. Proc. IDW'18. 2018, p.308.
4) Y. Goto et al. Tech_library KOBELCO research institute. 2020, No.50, pp.21-24.
5) Thin Film Materials and Devices Research Group ed. Thin Film Transistors. CORONA PUBLISHING CO., LTD., 2008, p.229
6) J. Park et al. Appl. Phys. Lett. 2008, Vol.93, pp.053501-1-053501-3.
7) H. Lu et al. Proc. 2016 23rd International Workshop on Active-Matrix Flatpanel Displays and Devices. 2016, pp.131-134.
8) Y. Magari et al. ECS J. Solid State Sci. Technol. 2017, Vol.6, pp.Q101-Q107.
9) H. Tsuji et al. IDW '20. 2020, pp.149-150.
10) N. Morosawa et al. Jpn. J. App. Phys. 2011, Vol.50, Article096502.
11) T. Liang et al. IEEE J. Electron Devices Soc. 2018, Vol.6, pp.680-684.
12) Z. Ye et al. IEEE Tran. Electron Devices. 2012, Vol.59, pp.393-399.
13) R. Chen et al. IEEE Electron Device Lett. 2012, Vol.33, pp.1150-1152.
14) M. Nakata et al. IEEE Transactions on Industry Application. 2017, Vol.53, pp.5972-5977.
15) M. Nakata et al. Jpn. J. Appl. Phys. 2019, Vol.58, No.9, Article090602.
16) S. Morita et al. R&D Kobe Steel Engineering Reports. 2015, Vol.65, No.2, pp.72-77.
17) J. Wu et al. IEEE Transactions on Electron Devices. 2021, Vol.68, Issue12, pp.6617-6622.