

Hall Mobility Manipulation in TiO_{2-x} Semiconductor Films by Hydrogen-ion Irradiation

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The effects of different irradiation doses of hydrogen ions on TiO_{2-x} semiconductor films were investigated. The total doses were controlled between $\sim 10^{14}$ and $\sim 10^{15}$ atom/cm² at an acceleration energy of 110 keV. The Hall mobility was manipulated by changing the irradiation dose while the carrier concentration was not. The amorphous crystal structure was consistently maintained upon irradiation. The electronic structures of the molecular orbitals in the conduction band were modified, and the band edge states below the conduction band increased with increasing irradiation dose. These changes in electronic structure were correlated to the chemical bonding states and could lead to variations in the Hall mobility without a structural transformation.

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I. INTRODUCTION

Oxide semiconductor-based thin-film transistors (Ox-TFTs) are potential replacements for existing Si-based TFTs in electrical and optical devices because they can be flexible, lightweight and mechanically robust, allowing electronic displays and other devices to be fabricated on plastic substrates. OxTFTs with active channel layers of oxide semiconductors such as ZnO and InGaZnO typically show high mobility and stability [1,2]. Despite their excellent performances, oxide semiconductors require complex stoichiometries, which complicates synthesis, and expensive indium, which limits mass application. These drawbacks can be overcome using a simple compositional oxide with controllable and efficient properties.

Titanium oxide (TiO_{2-x}) is a versatile material for use as a transparent conducting oxide (TCO) or a transparent oxide semiconductor (TOS) due to its highly-suitable physical and chemical properties, such as high transmittance in the visible region, low resistivity, high mobility,

high refractive index (2.75 at 550 nm), and high dielectric constant (~ 170) [3-7]. The photoelectric and the photochemical properties of TiO_2 thin films have allowed them to be successfully used in solar cells [8], optical filters [9], gas sensors [10], and photocatalysts [11]. TiO_{2-x} is less expensive than indium-based oxides such as indium tin oxide (ITO) and InGaZnO, which are current promising TCO and TOS materials. As a result, much work has sought to develop facile methods to control these materials' characteristics. Annealing, ion implantation and other treatments have been tried [12]. Annealing requires high temperatures to transform the crystal structure and is not suitable for the development of flexible devices that need low-temperature processing. Ion implantation induces physical structural damage in the grown film and requires a subsequent curing process such as annealing.

Ion irradiation using a light element such as hydrogen is a suitable method for manipulating the physical and the electrical properties while causing minimal damage to the material. The introduction of structural disorder, defects, and columnar amorphization depends upon the extent of the electronic energy loss mecha-

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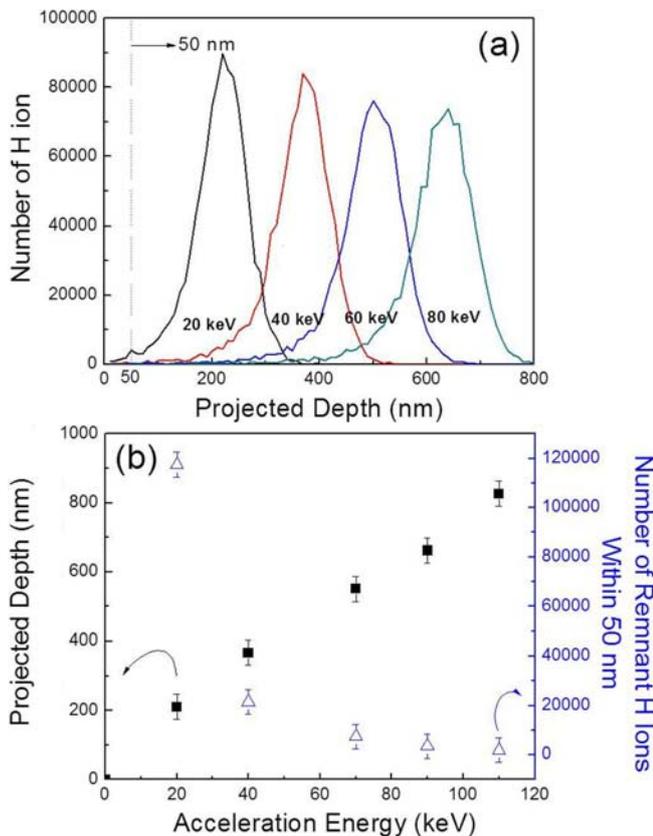


Fig. 1. (Color online) (a) Simulated trajectories of hydrogen ions in TiO_{2-x} film for various ion acceleration energies, as calculated using the stopping and range of ions in matter (SRIM) code. (b) Calculated projected depths of hydrogen ions and the number of remnant hydrogen ions within 50-nm TiO_{2-x} as functions of the acceleration energy.

nism [13]. Ion irradiation can also induce a crystalline-to-crystalline phase transition instead of causing amorphization or structural damage [14]. Our previous study on hydrogen-ion irradiation of ZnO films showed a dramatic enhancement of the Hall mobility with a change in the electronic structure, but not in the physical structure [15].

This letter proposes manipulation of the Hall mobility of TiO_{2-x} films at room temperature through hydrogen ion irradiation without inducing a structural transformation. The changes in the electrical properties are explained through a systematic analysis of the electronic structure and the chemical bonding states after different irradiation doses of hydrogen ions.

II. EXPERIMENT

TiO_{2-x} films, 50-nm thick, were RF-sputtered onto thermally-grown SiO_2 (100 nm) at a 100-W RF power. An oxygen-deficient 3-in. TiO_{2-x} target (dark gray color) was used, and the process pressure was maintained

at 10 mTorr by using an Ar gas flow of 50 sccm. Hydrogen ions were irradiated onto the TiO_{2-x} thin films at 110 keV by using a 2-MeV tandem accelerator. The doses of hydrogen ions were in the range $10^{14} - 10^{15}$ atoms/cm². The ion beam size was 140 mm², with a current density of $\sim 30 \mu\text{A}/\text{cm}^2$. Figure 1(a) shows simulated trajectories of hydrogen ions in TiO_{2-x} films at different ion acceleration energies. The trajectories were calculated using the stopping and range of ions in matter (SRIM) code. The simulated dose was fixed at 10^8 atoms/cm². The simulated results can be used to estimate the effects of dose for $10^{14} - 10^{15}$ atoms/cm². From the simulation results, the projected depth of the hydrogen ions and the number of hydrogen ions remaining within the 50-nm TiO_{2-x} were calculated at different acceleration energies (Fig. 1(b)). An acceleration energy of 110 keV was shown to be adequate for hydrogen ions to pass completely through the 50-nm TiO_{2-x} film and not to become incorporated in the films. The physical damage caused by the accelerated ions was minimized due to their light mass.

Changes of the irradiated films' electrical properties were assessed through Hall measurements using a van der Pauw configuration with a permanent magnet of 0.55 Tesla at room temperature. A comparison of the relative quantities of remnant hydrogen in the films was performed by using elastic recoil detection (ERD) with a 2 MeV He ions [16]. The ERD methods consisted of measuring the energy spectrum of protons that had been elastically hit by incident He ions and recoiled in a forward direction. Changes in the crystal structure were analyzed by using X-ray diffractometry (XRD) and transmission electron microscopy (TEM). The composition was investigated by using Rutherford backscattering (RBS) and X-ray photoelectron spectroscopy (XPS). The RBS measurement was performed using 2-MeV He^{++} ions with a scattering angle of 170° . Chemical bonding states were also examined by using XPS with a monochromatic Al K α source with a pass energy of 20 eV. Electronic structures in the films' conduction bands were measured by using X-ray absorption spectroscopy (XAS) with the coherent X-ray beam source at the Pohang Accelerator Laboratory (PAL) on beamline 7B1. Band gaps and band edge states below the films' conduction bands were examined at incident angles of 65° , 70° , and 75° at photon energies of 0.75 – 6.4 eV by using spectroscopic ellipsometry (SE) with a rotating analyzer system and an auto retarder.

III. RESULTS AND DISCUSSION

The films' carrier concentration and Hall mobility were measured before and after hydrogen-ion irradiation (Fig. 2). Before irradiation, the TiO_{2-x} film had a carrier concentration and mobility of $4.96 \times 10^{13} \text{ cm}^{-3}$ and $14.77 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. Upon irradiation, the carrier concentration changed little while the Hall mo-

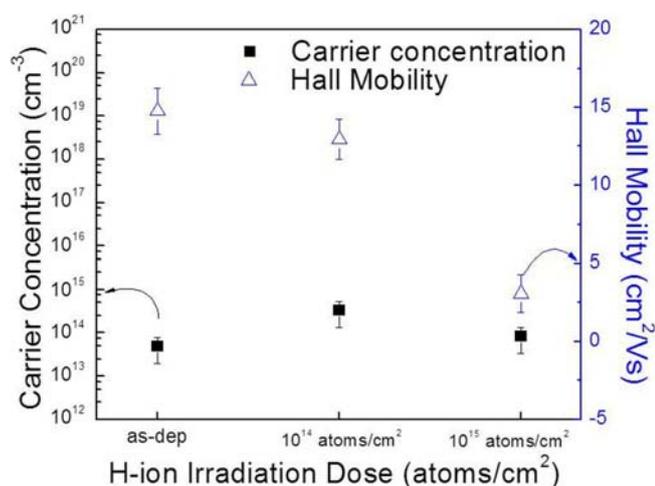


Fig. 2. (Color online) Carrier concentration and Hall mobility of TiO_{2-x} films as functions of the hydrogen-ion irradiation dose.

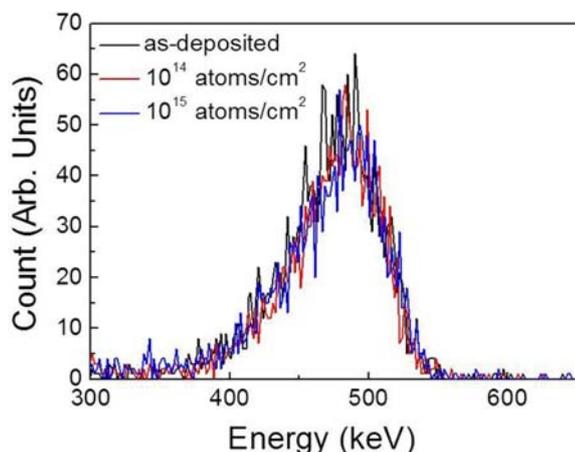


Fig. 3. (Color online) ERD spectra of hydrogen-irradiated TiO_{2-x} films for various hydrogen-ion irradiation doses. The spectrum of the as-deposited TiO_{2-x} film is also plotted to allow a comparison with hydrogen-ion-irradiated 50-nm TiO_{2-x} film.

bility greatly decreased to $3.08 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ after irradiation at $10^{15} \text{ atoms/cm}^2$. Hall mobility was tunable via the irradiation dose; the factors responsible for the changes will be discussed with respect to the physical and the electronic structures.

In order to analyze the remnant hydrogen after hydrogen-ion irradiation, we performed an ERD analysis as shown in Fig. 3. As-deposited TiO_{2-x} films were simultaneously measured to compare with the relative changes in hydrogen contents within the TiO_{2-x} films as the irradiation dose of hydrogen ions was increased. As the irradiation dose was increased to $10^{15} \text{ atoms/cm}^2$, the relative amount of remnant hydrogen changed little. These results mean that hydrogen from hydrogen-ion irradiation at an acceleration energy of 110 keV dose not remain in the film, similar to the simulation results in

Table 1. Change in the stoichiometry of as-deposited and hydrogen-ion-irradiated TiO_{2-x} films, as measured by using RBS and XPS.

Hydrogen ion dose	RBS		XPS	
	Ti	O	Ti	O
as-dep.	1	1.9	1	1.8
$1 \times 10^{14} \text{ atoms/cm}^2$	1	2.0	1	1.9
$1 \times 10^{15} \text{ atoms/cm}^2$	1	2.4	1	2.3

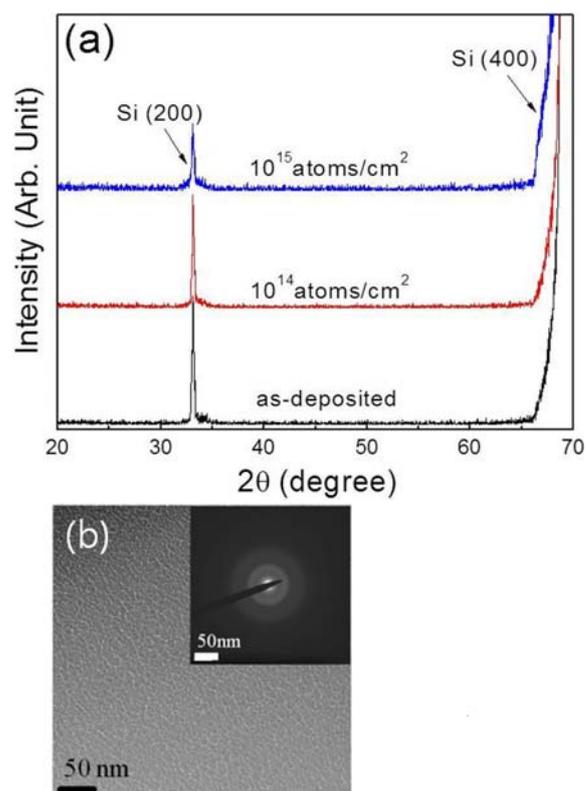


Fig. 4. (Color online) (a) XRD data measured for as-deposited and hydrogen-ion-irradiated TiO_{2-x} films for various hydrogen-ion irradiation doses. (b) Plane-view bright-field TEM image of an as-deposited TiO_{2-x} film.

Fig. 1.

XRD was used to observe the films' crystal structures (Fig. 4(a)). After irradiation, crystalline features related to TiO_{2-x} diffraction peaks were not observed and an amorphous structure was maintained. The detailed local structure was also examined by using a plane-view bright-field TEM image (Fig. 4(b)) of the as-deposited TiO_{2-x} film, which shows an amorphous structure similar to that of the XRD spectra. Therefore, hydrogen-ion irradiation at 110 keV did not physically alter the films' crystalline structure.

Table 1 represents the changes in the stoichiometry of the TiO_{2-x} films as a function of the hydrogen-ion irradiation dose, as measured by using RBS and XPS. As the irradiation dose was increased, the relative composi-

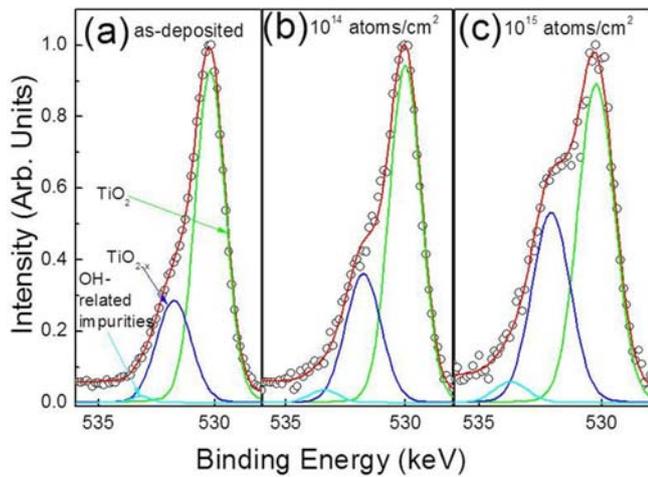


Fig. 5. (Color online) O $1s$ XPS core-level spectra of TiO_{2-x} films irradiated with hydrogen ions at (a) 0 atoms/cm² (as-deposited) (b) 10^{14} atoms/cm² and (c) 10^{15} atoms/cm².

tion of oxygen changed from oxygen-deficient TiO_{2-x} to oxygen-rich TiO_{2+y} in both measurement results. This means that the irradiation can cause oxidation by local atomic heating based on the electronic stopping energy loss mechanism of the light hydrogen ion [17]. In addition, an increase in the oxygen coordination is able to generate chemical oxygen bonding states.

The detailed chemical oxygen bonding states were analyzed through O $1s$ XPS spectra (Fig. 5). Surface contamination by adsorbed OH, C, H₂O, *etc.* and preferred sputtering of light elements were minimized by sputtering using Ne ions at 500 eV. Considering previous research, the O $1s$ spectra were deconvoluted into three Gaussian peaks with the subtraction of a Shirley-type background [18]. The peak at the lowest binding energy was attributed to O^{2-} ions in metal oxides, indicating TiO_2 bonds. The peak at the highest binding energy, around 533.5 eV, was attributed to chemisorbed or dissociated oxygen or OH species on the film's surface, such as $-\text{CO}_3$, adsorbed H₂O or adsorbed O_2 [19, 20]. The component peak at medium binding energy was associated with OH bonding species and with O^{2-} ions in the oxygen-deficient TiO_{2-x} bonding matrix. This oxygen-deficient TiO_{2-x} bonding state appeared to increase with increasing hydrogen-ion irradiation dose. The XPS results show that hydrogen-ion irradiation increased the oxygen-deficient TiO_{2-x} chemical bonding state, which is correlated to the increased oxygen stoichiometry previously shown in Table 1.

An XAS analysis of the O K_1 edge was used to examine the films' electronic structures related to changes in the conduction band and the molecular orbital ordering. The spectra were normalized in order to observe the relative changes of the molecular orbital structure in the conduction band. The normalization was to subtract an X-ray beam background from raw data; the differences

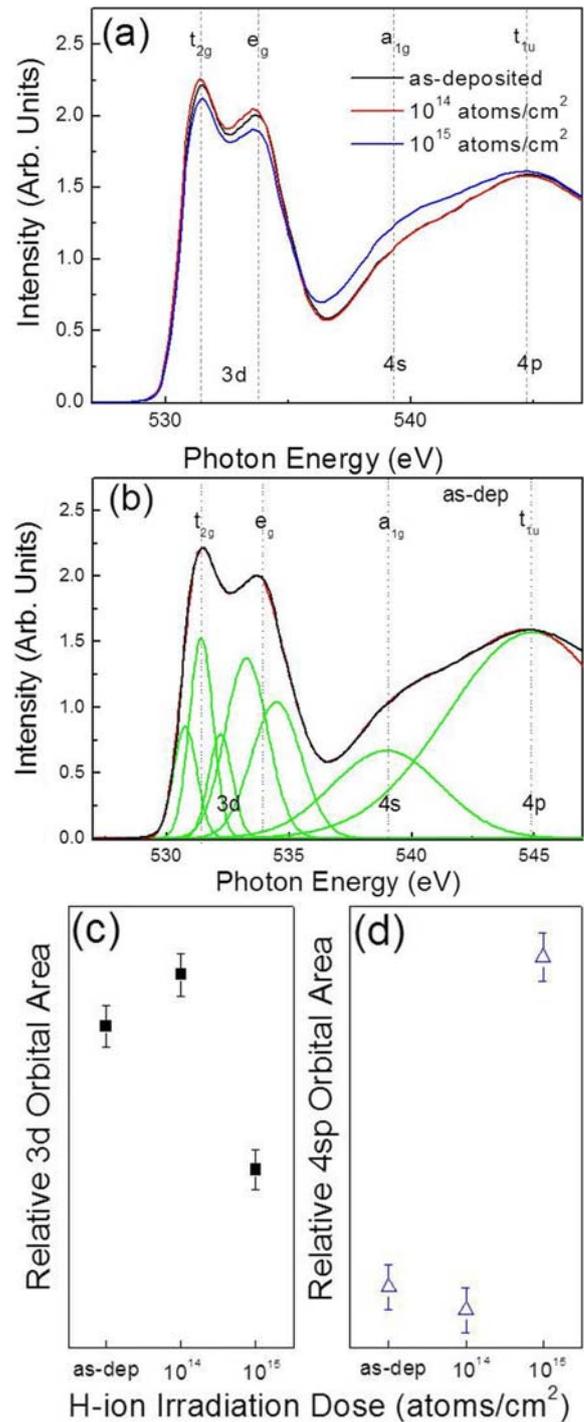


Fig. 6. (Color online) (a) Normalized XAS O K_1 edge spectra, (b) Gaussian fitting results of the O K_1 edge spectra for the as-deposited TiO_{2-x} film, (c) relative 3d orbital area, and (d) relative 4sp orbital area calculated by using the Gaussian fitting results in (b).

between the pre- and the post-edge levels were scaled to an arbitrary, but uniform, value [21]. The O K_1 edge spectra were fitted to Gaussian curves to compare qualitative changes of molecular orbital hybridization between

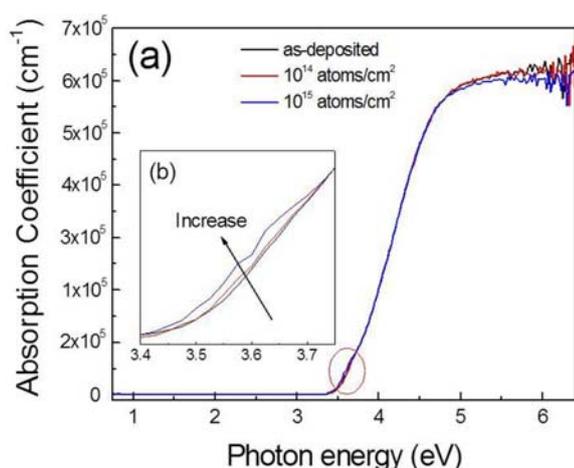


Fig. 7. (Color online) (a) Absorption coefficients of variously irradiated TiO_{2-x} films, and (b) enlargement of the band edge state below the conduction band.

titanium and oxygen. The Gaussian fits comprise Ti $3d$ t_{2g} states with threefold degeneracy, Ti $3d$ e_g states with twofold degeneracy, and two features corresponding to Ti $4s$ and Ti $4p$ states based on the octahedral symmetry [22]. Figure 6(a) shows the normalized oxygen (O) K_1 edge spectra, and Fig. 6(b) shows the Gaussian fits for the molecular orbital structure of the as-deposited TiO_{2-x} film. After irradiation, no distinct molecular orbital splitting of the TiO_{2-x} $3d$ orbitals was observed. However, the qualitative area of the conduction band related to $3d$ and $4sp$ orbitals changed slightly with increasing hydrogen irradiation dose. The Gaussian fits in Fig. 6(b) were used as the basis of the comparison of the calculated $3d$ and $4sp$ orbital areas in Figs. 6(c) and (d). As the irradiation dose was increased, the relative area of the $3d$ orbital decreased and that of the $4sp$ orbital increased. The directionality of the d molecular orbital, rather than that of the spherically symmetric s molecular orbital was dominant, when considering the features of the molecular orbital structure of TiO_{2-x} . The shrinkage in the conduction band area of the directional d orbital ordering with increasing irradiation dose could have degraded carrier transport by decreasing the unoccupied conduction-band states and the directionality of the molecular orbital ordering [15].

Band-edge states below the conduction band were investigated through SE spectra in the range 0.75 eV – 6.4 eV (Fig. 7). The optical band gap of the variously-irradiated films showed no changes near ~ 3.7 eV. However, the band-edge states below the conduction band were slightly increased with increasing irradiation dose. The band-edge states, generally interpreted as defect states in the electronic band diagrams, can degrade mobility due to charge trapping and increased charge scattering during charge transport. XAS and SE results suggest that the degradation of the Hall mobility with increasing hydrogen ion irradiation was due to modifica-

tions of the electronic structure in the conduction band and of the band-edge states below the conduction band, which were caused by the increase in the number of oxygen deficient chemical bonding states in the films.

IV. CONCLUSION

TiO_{2-x} semiconductor films were irradiated with various doses of hydrogen ions at 110 keV. Hydrogen-ion irradiation allowed the Hall mobility to be tuned between $3.08 \text{ cm}^2/\text{Vs}$ and $14.77 \text{ cm}^2/\text{Vs}$ without any change in the carrier concentration. Even though the irradiation did not physically alter the structure with the increasing irradiation dose, it did induce oxidation by increasing the number of oxygen - deficient states. Changes in the electronic structure-molecular orbital structure and band edge states below the conduction band - were observed with increasing irradiation dose. The number of unoccupied states in the conduction band increased due to a distortion of the $3d$ and the $4sp$ molecular orbitals, and the band edge states below the conduction band also increased. The changes in the electronic structure were correlated to the increases in the numbers of chemical bonding states related to oxygen-deficient TiO_{2-x} . The modulation of the Hall mobility was attributed to changes in the electronic structure near the conduction band caused by changes in the chemical bonding states of oxygen. This research suggests that hydrogen-ion irradiation may be a promising method for manipulating the Hall mobility of an oxide semiconductor without a need for either additional heating or a physically structural transformation.

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