Crystal Phase-selective Growth of Nb-doped TiO2 Thin Films by the Helicon-Wave-excited-Plasma Sputtering Method

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論 文 内 容 要 旨

There are two original studies in this doctoral thesis. First, I succeeded in the fabrication of annealing-free Nb-doped transparent anatase TiO_2 (A-TiO_2:Nb) films on alkaline-free glass substrates by helicon-wave-excited-plasma sputtering (HWPS). The films tended to crystallize in the stable electrically semi-insulating rutile phase. However, although the appropriate deposition condition window was narrow, the deposition temperature higher than 450 °C and O_2 partial pressure PO_2 in the range between 5×10^{-4} and 1×10^{-2} Pa, enabled the deposition of a high refractive index semi-conducting anatase phase. Anatase $Ti_{0.907}Nb_{0.093}O_2$ film deposited at 500 °C and PO_2= 5×10^{-4} Pa exhibited a resistivity of 3.4×10^{-3} Ω·cm and an optical transmittance higher than 90%. The refractive index of A-TiO_2:Nb was found to be approximately 2.63 at 450 nm with spectroscopic ellipsometry, which is comparable to the InGaN alloys.

Secondly, crystal phase-selective epitaxy of TiO_2:Nb film on GaN is demonstrated using helicon-wave-excited-plasma sputtering epitaxy (HWPSE) for the first time. On the clean (0001) GaN, rutile (100) TiO_2:Nb was grown regardless of growth temperature T_g. On the (0001) GaN covered with a monolayer-thick (100) or (001) β-Ga_2O_3, anatase (001) A-TiO_2:Nb films were grown under high T_g and low O_2 partial pressure conditions. The transmittance between 450 and 900 nm for the 200-nm-thick films was approximately 80%. Typical resistivity of the A-TiO_2:Nb/GaN hetero-structure was as low as 3.6×10^{-4} Ω·cm, due to the interfacial conduction.

Transparent conducting oxides (TCOs) are a key component in many optoelectronic devices including flat panel displays, smart displays, and photovoltaic devices. Recently, A-TiO_2:Nb films are attracting attention as a new TCO. The values of σ and T of A-TiO_2:Nb were comparable to those of Sn-doped In_2O_3. A-TiO_2:Nb is more suitable for TCO than rutile one due to its higher mobility and larger Bohr's radius.

Sputtering methods can prepare large-area films of well controlled compositions economically. However, the surface damage caused by high energy sputtering particles is a critical issue. To overcome the problem, our group has been developing a newly designed deposition technique using a helicon-wave-excited-plasma (HWP), which can be excited in relatively high-vacuum and generates high-density low-energy plasma. From a practical point of view, direct growth of TiO_2:Nb polycrystalline films on heated substrates is preferable because such a process is more cost effective. However, A-TiO_2:Nb polycrystalline films directly grown on glass tend to show ρ values much higher than films produced by the thermal annealing method. The lowest ρ value reported in the literature is $\rho = 1.7\times10^{-2}$ Ω-cm, which is too high for practical use. Hence, direct fabrication of highly conducting TiO_2:Nb polycrystalline film on glass is a challenging issue.

In chapter 4, I explained the critical importance of very low oxygen partial pressure for emerging semiconducting property in anatase phase TiO_2:Nb-visible-transparent films on alkaline-free glass substrates was described

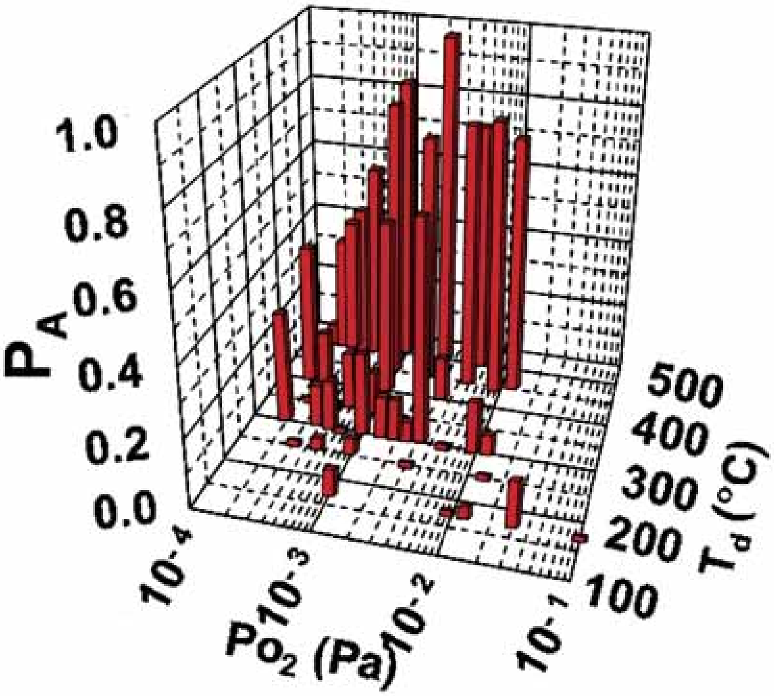

Fig.1. The panel shows the three dimensional (3D) representation of the ratio of anatase to rutile phase (P_A) in the $Ti_{1-x}Nb_xO_2$ films ($x = 0.057$ and 0.093) as functions of T_d and PO_2, where PO_2 is a product of P_d and $f(O_2)$.

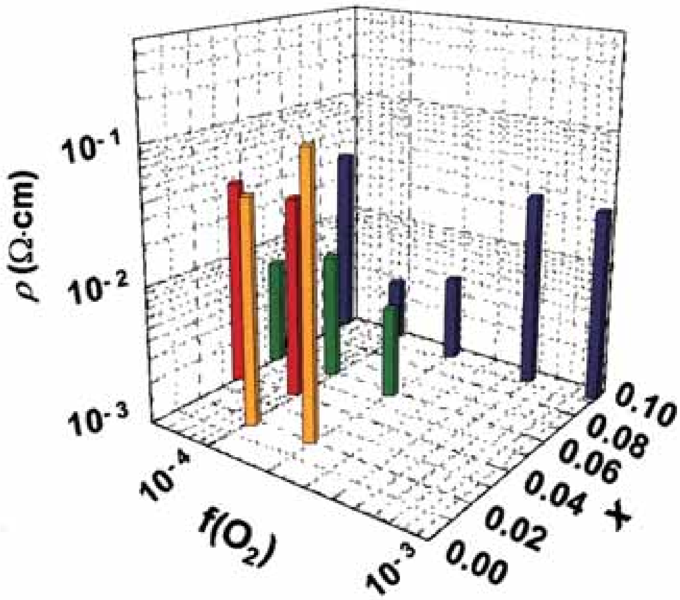

Fig.2. 3D representations of resistivity for the A-TiO_2:Nb films as functions of NbO_2 mole fraction x and $f(O_2)$. The films were grown at T_d= 500 °C and P_d= 5 Pa.

for the unique, post-deposition annealing-free HWPS method. The TiO_2:Nb films tended to crystallize in the stable rutile phase, as is the case with PLD and other deposition methods. Because rutile TiO_2 (R-TiO_2) is an insulating material, depositing A-TiO_2 is necessary for obtaining TCO films. To find the deposition window for obtaining A-TiO_2, the crystal structure was examined as functions of T_d, P_d, and PO_2 which change the degree of oxidation. As PO_2 is a product of P_d and $f(O_2)$, the ratio of anatase to rutile phase (P_A) of the films is summarized as functions of T_d and PO_2 using a three-dimensional representation in Fig.1. The deposition condition window suitable for reasonably semi-conducting A-TiO_2:Nb film fabrication was very low PO_2 (5×10^{-4}~1×10^{-2} Pa), and high T_d (450~500 °C) conditions. As far as anatase phase was maintained by the crystal phase-selection, the electron concentration and resistivity increased and decreased, respectively, with the increase in Nb concentration up to x= 0.093, when $f(O_2)$ was properly controlled between 0.005 and 0.02 % (T_d= 500 °C, P_d= 5 Pa). According to the surface-damage-free property of the remote plasma-type HWPS method, smooth A-TiO_2:Nb (and R-TiO_2:Nb as well) films were obtained. The root-mean- square (RMS) roughness values for the A-$Ti_{1-x}Nb_xO_2$ films were as small as 1~2 nm, which are similar to the A-TiO_2 films deposited by the reactive dc magnetron sputtering and PLD methods. Because neither the seeding layer for obtaining the most conducting (001) orientation A-TiO_2:Nb nor H_2 annealing was used throughout this study, the lowest ρ value was 3.4×10^{-3} Ω-cm [x = 0.093 and $f(O_2)$= 0.01 %], n= 2.2×10^{21} cm^{-3}, and μ_H = 2.8 cm^2/V·s.

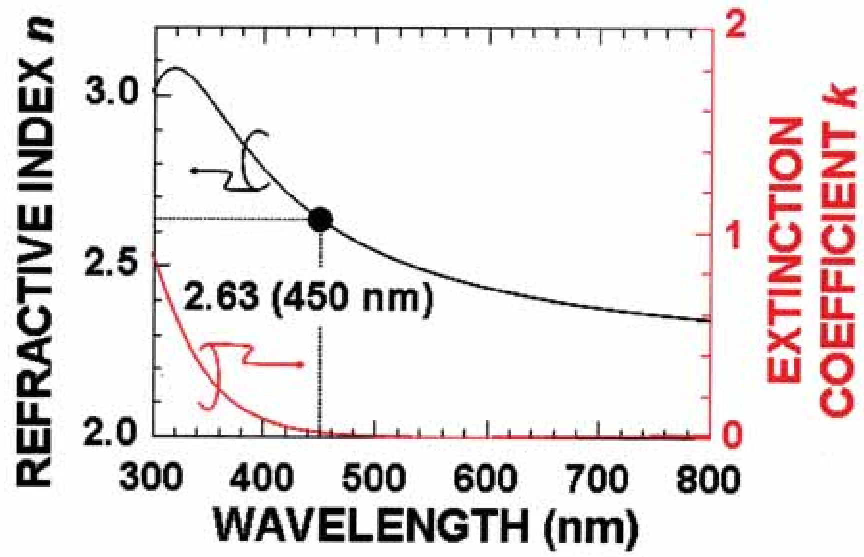

Fig.3. Representative spectroscopic ellipsometry results (refractive index and extinction coefficient) for the 255-nm-thick $Ti_{0.907}Nb_{0.093}O_2$ film deposited by HWPS at T_d= 500 °C, P_d= 5 Pa, and $f(O_2)$= 0.02 %.

Simultaneously, transparent (T > 85 %) property and index- matching to GaN (~2.63 at 450nm) were demonstrated as shown in Fig.3. In order to verify the transmittance values and to obtain the dispersion relations for refractive index n and extinction coefficient k, spectroscopic ellipsometry was used and representative results for a 255-nm -thick A-$Ti_{0.907}Nb_{0.093}O_2$ film on a glass substrate are shown in Fig.3. In analyzing the raw data, Kramers- Krönig model was employed. From Fig.3., n was determined to be approximately 2.63 at λ= 450nm and 2.55 at λ= 500nm. These values are not far from those of GaN being 2.48 and 2.43 at 450 and 500nm, respectively.

In chapter 5, I demonstrated the selective epitaxial growth of rutile and anatase TiO_2:Nb films on GaN templates by the HWPSE technique. GaN-based technology has lead to an explosive growth in optoelectronics, triggered by the invention of blue light emitting diodes (LEDs) and blue laser diodes. The first step for applying the novel electric and optical properties of TiO_2:Nb to GaN-based blue LEDs is to fabricate A-TiO_2:Nb films on a *p*-type GaN (0001) film. Approximately 200-nm-thick TiO_2:Nb epilayers were grown using the HWPSE apparatus on a 3-μm thick (0001) GaN epitaxial template, which was grown on a (0001) Al_2O_3 substrate by metal-organic vapor phase epitaxy. The NbO_2 mole fraction x of the sintered $Ti_{1-x}Nb_xO_2$ target was 0.057. The crystal phase of the epilayer could be controlled by the pre-treatment procedure on the GaN surface. On the GaN template cleaned and etched with a HCl dipping, purely rutile (100) TiO_2:Nb films were grown. The results indicate that the insertion of a thin Ga-O layer either by thermal oxidization or by growing Ga_2O_3 sheet layer changed both the crystal phase and epitaxial relationship. Representative 2θ-ω x-ray diffraction (XRD) patterns for the TiO_2:Nb films grown on the etched and Ga_xO_y-covered (0001) GaN templates are shown in Fig.4. On the etched GaN, (100) R-TiO_2:Nb grew regardless of T_g, between room temperature and 520 °C, as shown for example by the bottom trace. Conversely, the (004) A-TiO_2 diffraction peak appeared in addition to (200) R-TiO_2 peak for the film grown on the Ga_xO_y-covered (0001) GaN. The rutile (100) TiO_2:Nb films grew on the etched clean (0001) GaN surface with the in-plane epitaxial relationship [010] TiO_2 // [10-10] GaN. While, the anatase (001) TiO_2:Nb films grew on appropriately oxidized (0001) GaN with the in-plane relations [110] TiO_2 // [10-10] GaN (and [110] TiO_2 // [11-20] GaN) under high temperature and low oxygen partial pressure conditions. A-TiO_2 may grow with (001) A-TiO_2//(0001) GaN and <110> A-TiO_2//<010> Ga_2O_3//<11-20> GaN. A monolayer- thick Ga_xO_y insertion is shown to convert the crystal phase and orientation of the overgrown TiO_2:Nb epilayer from (100) rutile to (001) anatase.

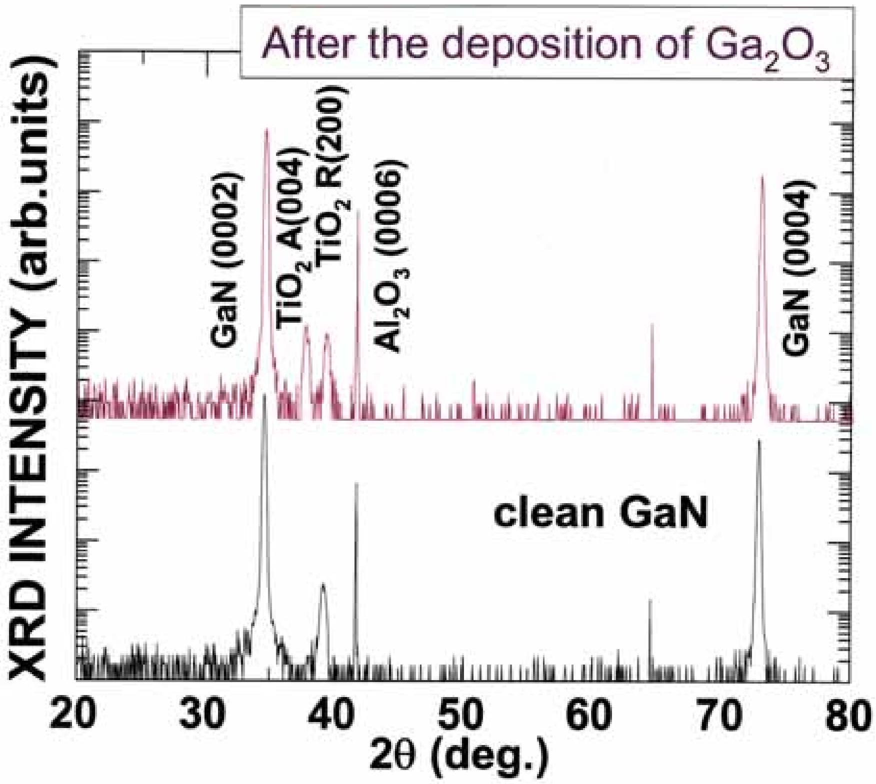

Fig.4. Representative 2θ-ω XRD patterns for TiO_2:Nb epilayers grown on etched and Ga_xO_y-covered (0001) GaN templates. The designed Ga_2O_3 thickness was 0.6 nm.

論文審査結果の要旨

掲記論文は、新規な高屈折率透明導電性酸化物（ＴＣＯ）薄膜用材料として期待されている「アナターゼ型ニオブ添加二酸化チタン（TiO_2：Ｎｂ）」薄膜の、ガラス上への堆積および窒化ガリウム（ＧａＮ）上へのエピタキシャル成長を、安価な装置構成で再現性良く可能にする独自のスパッタリング堆積法である「ヘリコン波励起プラズマスパッタ(HWPS)法」にて行い、絶縁相であるルチル型TiO_2：Ｎｂとの結晶相選択的製膜を可能としてエレクトロニクス工学分野に対して寄与しようとするものである。

二酸化チタンの研究の歴史は古く、ルチル、アナターゼ、ブルッカイト等の結晶相があり、光触媒や紫外線遮断フィルター、化粧品などとして一部実用化されているものもある。特に、屈折率が高く安定構造であるルチル型の場合は絶縁性に優れるため、いわゆる高誘電率（high-k）ゲート材料としての研究もなされている。一方、近年、アナターゼ型TiO_2の IVa 族Ｔｉサイトに Va 族のＮｂを添加し、水素（還元）雰囲気中で熱処理を施すことによって導電性が出現することが明らかになり、各種製膜法によって「高屈折率ＴＣＯ」なる新たな物質の創成研究が開始された。

本論文では、従来必要とされていた還元雰囲気での熱処理を用いることなくTiO_2のＴＣＯ薄膜を得るため、活性プラズマによる表面損傷を最小限に抑え、高品質な大面積半導体薄膜を得る技術として独自に開発してきた HWPS 法を用い、ガラス基板上への結晶相選択的堆積、および発光ダイオードへの応用を鑑みたＧａＮ上への結晶相選択的エピタキシャル成長を行った結果を述べている。

まず、低抵抗率アナターゼ型TiO_2薄膜をガラス基板上に堆積するための条件として、比較的高温で非常に低い酸素分圧雰囲気での成長が適することを明らかにし、電気特性制御における Nb 添加量や酸素分圧依存性に関する考察を行った結果、水素熱処理を行うことなく 3×10^{3} Ω·cm の低抵抗率薄膜を得た。また、通常何もしなければルチル型TiO_2しか堆積することができないＧａＮ上に、アナターゼ相を選択的にエピタキシャル成長させる技術として、１原子層程度の酸化ガリウム層の挿入が有効であることを示し、ＧａＮ上に世界で初めてアナターゼ型TiO_2：Ｎｂのエピタキシャル成長に成功した。

温度や酸素分圧による結晶相の制御、また、エピタキシャル効果を用いた、一原子層程度の制御層挿入によるエピタキシャル層の結晶相の制御など新規なデータも多く、それらを表面科学に基づいて説明しており、審査にあたった教授全員が合格の判定をした。

よって、本論文は博士(工学)の学位論文として合格と認める。