博士学位論文審査要旨

2023年7月18日

論 文 題 目：Water Vapor in DC Reactive Magnetron Sputtering Plasma: Characteristics and Applications
（反応性マグネトロンスパッタリングプラズマ中の水蒸気：特徴と応用）

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要　　旨：

反応性プラズマの基礎過程を調査する上で、水蒸気プラズマを用いることにより、特殊なガス処理設備を用いることなくプラズマ体積過程やプラズマ固体表面相互作用の研究が可能となる。しかしながら壁への吸着や、狭隘流路での固化、さらに電極上の絶縁物形成などにより、安定した放電を維持することが難しかった。論文提出者は、真空容器やガス供給系の温度分布を調整することにより水蒸気プラズマを安定して維持できることを実証し、放電電力を時間変化させた際に得られる陰極電流波形が、電極表面での反応性気体のリサイクリングを考慮した計算モデルを用いて説明できることを明らかにした。完成した水蒸気放電システムと亜鉛ターゲットを組み合わせ、アルゴン希釈した水蒸気をプラズマ化して酸化亜鉛薄膜を作成し、その結晶性と可視光領域の透過率、導電性などを調査した。その結果、透明で高導電性の酸化亜鉛薄膜が、60%以上の高水蒸気比率のプラズマを用いて生成可能であることを見いだした。また、静電探針法と分光法を用いたプラズマの計測により、固体表面近傍のイオン密度が、水蒸気比率が大きい状態で高くなる実験結果を示し、導電性薄膜形成との関連について考察を加えている。さらに、薄膜の品質に大きな影響を及ぼすと考えられる正負イオンのエネルギー分布関数を測定し、イオン衝撃がプラズマ薄膜生成過程に与える効果の重要度について評価している。

本論文は、水蒸気プラズマを安定化する混合ガス制御系を実現し、それを用いることによりプラズマ中の電子体積素過程やプラズマ－表面相互作用の基礎反応について、詳細な調査が可能となることを報告している。また、構築した実験系を用いて行った基礎研究から得られた成果を整理し、まとめた結果を酸化亜鉛薄膜の形成に適用して、導電性を有する薄膜の実現に成功している。よってその学術的価値は博士（工学）（同志社大学）の学位論文として十分高いものと認める。

総合試験結果の要旨

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要　　　旨 :

本論文の提出者は本学大学院理工学研究科電気電子工学専攻博士課程（前期課程）を 2020 年 9 月に修了し、2020 年 9 月に本学大学院理工学研究科電気電子工学専攻博士課程（後期課程）に入学し、現在、在籍中である。

本論文の主たる内容は Plasma and Fusion Research, 17, 2406040 及び Journal of Physics, Conference Series, 2244, 012099 他 1 件の論文と 2 件の査読付き国際会議 Proceedings に掲載済みであり、既に十分な評価を受けている。2023 年 7 月 1 日午後 1 時より二時間に亘り、提出論文に関する博士論文公聴会が開かれた。公聴会講演後の全ての質問に対して論文提出者は明快に回答し、終了後の審査委員による学力確認のための口頭試験においても、提出者の十分な学力を確認することができた。論文提出者はタガログ語を母語とするが、発表の序論部分を日本語で、主要部分を英語で発表することにより、高い語学運用能力を有することを示した。以上、論文提出者の専門分野における学力及び語学力は十分であることを確認した。よって総合試験の結果は合格であると認める。

博 士 学 位 論 文 要 旨

論 文 題 目：

Water Vapor in DC Reactive Magnetron Sputtering Plasma: Characteristics and Applications

(反応性マグネトロンスパッタリングプラズマ中の水蒸気：特徴と応用)

氏　　名： CATAPANG ALLEN VINCENT BARABONA

要　　旨：

The use of water vapor plasma in a thin film deposition process realizes the addition of hydrogen (H) in the plasma. The added H in the thin film structure improved the film properties for oxides, such as zinc oxide (ZnO), by acting as a shallow donor dopant. By using water vapor plasma, the doping of ZnO with H onto the lattice to improve the film's conductivity and reduce lattice stresses can be realized, with intended applications in optoelectronics such as in transparent conductive electrodes. This dissertation investigated the application of water vapor as the reactive gas in a DC magnetron sputtering system. The deposition process was systematically investigated by exploring the different areas, from the introduction of water vapor, the bulk plasma, and the magnetron cathode surface, to the thin film substrate region. The reactive magnetron sputtering plasma was applied to a plasma source with a pulsed conduit-type extraction electrode.

In Chapter 2, the stable flow of water vapor into a low-pressure deposition system using a heated vaporization-driven reservoir was controlled using the temperature. Increasing the temperature increased the responsiveness of the water vapor reservoir as a gas source. The simulation of the reactive magnetron sputtering process through Berg's reactive sputtering model for water vapor plasma showed that adsorption-dependent parameters significantly affected the deposition process. The effect on the pressure behavior at different discharge parameters was investigated by fitting the time-resolved pressure curves to the model, and the gas admixture was determined as the most suitable form of process control for oxide formation at the substrate region.

In Chapter 3, the effect of the water vapor plasma on the target surface condition was investigated. The dominant surface processes at the target surface region are dependent. At the target center, the redeposition of material was strong compared to the target racetrack where the erosion of target material by sputtering was dominant. Redeposited layers with preferred crystallographic orientations were observed at low water vapor content, and oxide overlayers were detected at high water vapor content settings. The oxide formation and surface morphology were compared with in-situ laser differential reflectance measurements, and the trends were similar to the compound formation according to Berg's sputtering model. The laser differential reflectance incident at the center was determined to be a viable method for monitoring the target surface condition during the plasma operation.

In Chapter 4, the ZnO thin films were deposited at varying water vapor content in an Ar – H_2O gas admixture. The change in film properties related was correlated to the near substrate surface plasma parameters obtained from a single Langmuir probe. The addition of water to the plasma significantly changed the behavior of the plasma and the growth mechanism of the film. The transition between a metallic Zn film to ZnO was observed with 40% water vapor content, and transparent and conductive films was deposited (87.5% transmittance, $\rho = 1.2\ \Omega$ cm). The measure confirmed the shallow H donor doping phenomenon with water vapor plasma. The effect of deposition control by adding a substrate bias and temperature was investigated. The polarity of the substrate bias changed the incident charged species, while the bias magnitude

affected the incident energy. The film characteristics were directly linked to the ion and electron flux to the surface. The shallow donor doping and optical transparency were unaffected by the substrate bias. For substrate heating, increasing the substrate temperature resulted in a localized increase in ions near the surface. As the substrate temperature increased, the growth of multiple ZnO peaks was promoted at higher temperatures while the resistivity consistently decreased. The shallow donor doping of ZnO for films deposited using water vapor plasma was stable for the 20 to 140°C range.

In Chapter 5, the production of positive and negative ions in water vapor plasma was confirmed using optical emission spectroscopy and ion energy measurements. The production of Ar^+, H^+, Zn^+, O^+, and OH+ ions was confirmed from the atomic and molecular band spectra at the visible (400-1000 nm) and UV regions (200-500 nm). The relative intensities indicated that the maximum ion formation was at 40% water vapor content. The positive ion energy distribution across the water vapor settings had an average peak ion energy at ~5.4 eV and the addition of water vapor to the plasma increased the peak energy by ~0.26 eV. The negative ion energy distribution was significantly broader and at higher energies (~274 eV for the 20 to 100% settings). The negatively-biased target surface accelerated the negative ions by ~69 to 89% of the cathode discharge voltage.

In Chapter 6, a reactive magnetron sputtering plasma source with a pulsed, conduit-type extraction electrode was designed. The charged species transport to the differentially pumped downstream region was confirmed by quadrupole mass spectrometry (QMS). The pulsed conduit-type extraction electrode extracted Ar^+, H_2O^+, H_3O^+, and Zn^+ ions, and the intensities were dependent on the extraction electrode voltage frequency. Multiple plasma characterization techniques confirmed the proposed space charge-dependent extraction mechanism. The simulation of the ion transport trajectories showed that plasma at the conduit volume was dependent on the condition at the plasma source and the extraction electrode voltage frequency. The ion current peaked at varying frequencies depending on the position inside the conduit volume. The electron saturation current steadily decreased as the frequency increased, indicating the possibility of electron trapping. The positive space charge in the conduit volume accelerated the ions further to higher energies than that set by the extraction electrode voltage (1 kHz to 250 kHz), but the trapping of electrons steadily decreased the ion energy as the frequency increased (<250 kHz). The average ion current density measured by a shielded Faraday cup exhibited an average ion current density with a Gaussian profile centered at 171 kHz. For the time-resolved measurements, the indirect time-of-flight showed that the extraction electrode voltage could control the mass ratio of extracted ions, with lower voltages favoring heavier ions. The addition of water vapor significantly complicated the behavior of the ion extraction and negative ions were detected by the Faraday cup. A positive tailing pulse in the off phase realized an increased ion extraction density compared to a similar increase in the extraction electrode voltage. Chapter 7 stated the main results and the recommendations for future work.