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TAILORING MEMRISTIVE BEHAVIOR IN NIO THIN FILMS VIA POST-ANNEALING TIME AND ELECTRODE ENGINEERING

Annotation

Nickel oxide (NiO) thin films were synthesized by the sol–gel spin-coating method and annealed at 400 °C for 2 and 5 hours to investigate the effect of post-annealing time on their memristive behavior. Silver (Ag) and indium (In) were employed as top electrodes. The optical bandgap was determined via Tauc plot analysis using reflectance data. Structural properties were examined by X-ray diffraction (XRD), and the memristive switching behavior was characterized by current–voltage (I–V) measurements using a Keithley-2460 SourceMeter. It was found that both annealing time and electrode type significantly affect the switching behavior and material properties.

Key words: NiO, memristor, sol-gel.

ФОРМИРОВАНИЕ МЕМРИСТИВНОГО ПОВЕДЕНИЯ В ТОНКИХ ПЛЕНКАХ NiO ПУТЕМ ИЗМЕНЕНИЯ ВРЕМЕНИ ОТЖИГА И ВЫБОРА МАТЕРИАЛА ЭЛЕКТРОДА

Аннотация

Тонкие пленки оксида никеля (NiO) были синтезированы методом золь-гель центрифугирования и подвергнуты отжигу при 400 °C в течение 2 и 5 часов для изучения влияния времени постотжига на их мемристивное поведение. В качестве верхних электродов были использованы серебро (Ag) и индий (In). Оптическая ширина запрещенной зоны была определена с помощью анализа графиков Тауца на основе данных отражения. Структурные свойства исследовались методом рентгеновской дифракции (XRD), а мемристивное переключение - с помощью измерений ток–напряжение (I–V) с использованием прибора Keithley-2460 SourceMeter. Было установлено, что как время отжига, так и тип электрода значительно влияют на характеристики переключения и свойства материала.

Ключевые слова: NiO, мемристор, золь-гель.

QIZDIRISH VA ELEKTROD MATERIALINI BOSHQARISH ORQALI NiO YUPQA QAVATLARIDA MEMRISTIV XATTI-HARAKATNI SHAKLLANTIRISH

Annotatsiya

Nikel oksid (NiO) yupqa qatlamlari sol–gel aylantirish (spin-coating) usuli bilan sintez qilinib, 400 °C da 2 va 5 soat davomida termik ishlov berildi. Post-annealing (qayta qizdirish) vaqtining memristiv xatti-harakatga ta'sirini o'rganish maqsad qilingan. Yuqori elektrod sifatida kumush (Ag) va indiy (In) materiallari ishlatildi. Optik energiya oralig'i (bandgap) yutilish spektridan (reflectance) olingan Tauc grafiklari yordamida aniqlandi. Struktura xossalari rentgen difraksiyasi (XRD) orqali o'rganildi, memristiv xatti-harakat esa Keithley-2460 SourceMeter qurilmasi yordamida tok–kuchlanish (I–V) o'lchovlari orqali baholandi. Tadqiqot natijalari shuni ko'rsatdiki, qizdirish vaqti hamda elektrod turi o'tish xatti-harakati va material xossalariga sezilarli darajada ta'sir qiladi.

Kalit so'zlar: NiO, memristor, sol-gel.

Introduction. Nickel oxide (NiO) is considered a promising material for resistive switching (memristive) devices due to its wide bandgap, chemical stability, and simple stoichiometry [1]. Memristive devices, capable of non-volatile resistance switching, are key candidates for next-generation non-volatile memory (NVM) technologies owing to their scalability, low power consumption, and CMOS compatibility [2].

Among synthesis methods, the sol–gel spin-coating technique offers a simple and cost-effective approach to fabricate uniform NiO thin films [3]. Post-annealing critically affects film properties such as crystallinity, defect density, and grain size, thereby influencing switching behavior [4]. In particular, variations in annealing time can alter oxygen vacancy concentrations and metallic Ni cluster formation, which are central to the switching mechanism [5]. Additionally, electrode material selection impacts Schottky barrier formation, filament dynamics, and switching stability [6]. Ag electrodes, with high mobility, actively participate in filament formation, while In electrodes offer relatively inert behavior, affecting switching mechanisms differently [7]. In this work, NiO thin films were synthesized by sol–gel spin-coating and annealed at 400 °C for 2 and 5 hours to investigate the effects of annealing duration on structural, optical, and memristive properties. The influence of Ag and In top electrodes on switching behavior was also analyzed, providing insights into optimizing NiO-based memristive devices for future memory and neuromorphic applications.

Literature review. NiO thin films have been widely studied for memristive applications due to their wide bandgap (~3.6–4.0 eV) and intrinsic p-type conductivity from nickel vacancies [8]. Deposition methods like PLD, sputtering, CVD, and sol–gel spin-coating have been utilized to achieve tunable film properties [9].

Resistive switching is primarily attributed to the formation and rupture of conductive filaments comprising oxygen vacancies and metallic Ni clusters [10]. Post-deposition annealing significantly affects film crystallinity and defect states [11]. Moderate annealing (300–500 °C) enhances crystallinity, reduces organic residues, and optimizes vacancy concentrations, thereby modulating switching behavior [12].

Electrode engineering is critical; mobile metals such as Ag and Cu promote filamentary switching, whereas inert electrodes like InGa and Au encourage interface-type switching [13], [14]. The electrode/oxide interface influences switching voltages, stability, and endurance [15]. Simultaneous optimization of electrode material and annealing conditions is essential. Shorter annealing preserves higher vacancy levels, favoring filament conduction, while prolonged annealing enhances crystallinity and stabilizes switching [16]. Proper control over these parameters is key to advancing reliable, low-power NiO-based memristive devices.

Research Methodology. In this study, a systematic approach was employed to fabricate and characterize nickel oxide (NiO) thin films with tailored memristive behavior through precise control of post-annealing time and electrode engineering.

First, high-purity reagents were selected for the sol–gel synthesis process. Nickel acetate tetrahydrate ($Ni(CH_3COO)_2 \cdot 4H_2O$, 99%, Sigma-Aldrich) served as the nickel source, dissolved in 2-methoxyethanol ($CH_3OCH_2CH_2OH$, ≥99.3%, Sigma-Aldrich) with monoethanolamine (MEA, C_2H_7NO, 98%, Sigma-Aldrich) added as a complexing agent in a 1:1 molar ratio with nickel acetate. The precursor solution was magnetically stirred at 60 °C for one hour to achieve a homogeneous and transparent sol, and subsequently aged for 36 hours at room temperature to stabilize the chemical composition.

The sol was then deposited onto pre-cleaned monocrystalline silicon (Si) substrates using a spin-coating method at 3000 rpm for 30 seconds. Following each spin-coating cycle, the films were dried at 100 °C for 10 minutes and pre-heated at 275 °C for 15 minutes to remove organic residues. This deposition–drying cycle was repeated six times to achieve the desired film thickness, ensuring uniformity and controlled growth.

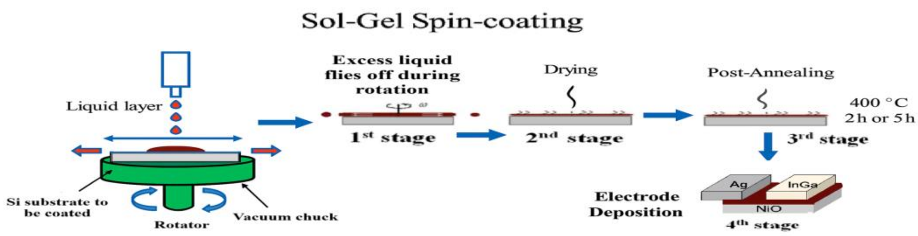
After deposition, post-annealing was performed in a muffle furnace at 400 °C for different durations - 2 hours and 5 hours - to systematically study the impact of thermal treatment on the structural, optical, and electrical properties. The samples were labeled as NiO-2h and NiO-5h, respectively.

For device fabrication, metal–insulator–metal (MIM) structures were assembled by depositing top electrodes of silver (Ag) and indium (In) onto the annealed NiO thin films, while the Si substrate served as the bottom electrode.

Comprehensive material characterization techniques were employed to analyze the resulting films. X-ray diffraction (XRD) measurements with Cu Kα radiation (λ = 1.5406 Å) were used to determine the crystallographic structure and phase purity. Memristive switching behavior was evaluated by current–voltage (I–V) measurements using a Keithley 2460 SourceMeter at room temperature, applying a double-sweep voltage from −5 V to +5 V.

Fig.1. NiO film preparation process scheme

Analysis and results. The structural, optical, and memristive properties of the NiO thin films were comprehensively analyzed to understand the effects of post-annealing time and electrode material on device performance. X-ray diffraction (XRD) patterns confirmed the polycrystalline nature of the NiO films, exhibiting reflections corresponding to the (111), (200), (202), (311), and (220) planes, characteristic of the cubic NiO phase (JCPDS Card No. 47-1049). Films annealed for 5 hours exhibited sharper and more intense diffraction peaks compared to the 2-hour annealed films, indicating enhanced crystallinity and larger grain growth due to the extended thermal treatment. Improved crystalline quality is beneficial for achieving better electrical properties in memristive devices, as it reduces defect density and enhances filament stability during resistive switching.



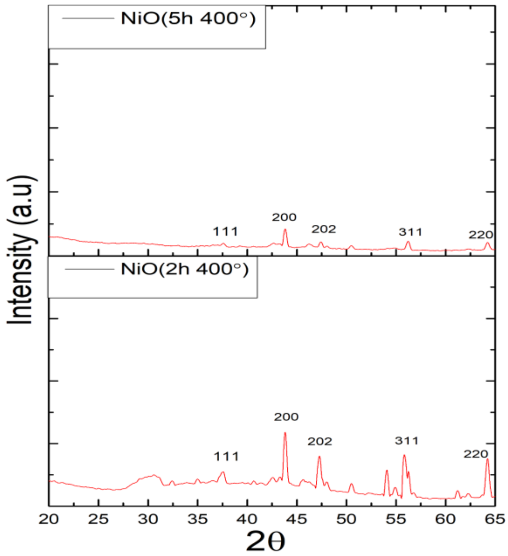


Fig.2- XRD patterns of NiO thin films deposited by sol–gel method on Si substrates and annealed at 400 °C for 2 and 5 hours

The optical bandgaps of the films were determined from Tauc plot analysis based on reflectance measurements. Direct bandgap transitions were observed for both samples, with extracted bandgap values of approximately 3.38 eV for the 2-hour annealed sample and 3.44 eV for the 5-hour annealed sample. The slight increase in bandgap with longer annealing time suggests reduced defect densities and improved structural ordering within the NiO lattice. Enhanced bandgap values further support the improved crystallinity indicated by the XRD results.

Current–voltage (I–V) measurements were performed to evaluate the memristive switching behavior of the fabricated devices. Typical bipolar resistive switching (BRS) behavior was observed in all devices. NiO films with Ag electrodes exhibited higher ON-state current levels and better switching stability compared to devices using In electrodes.

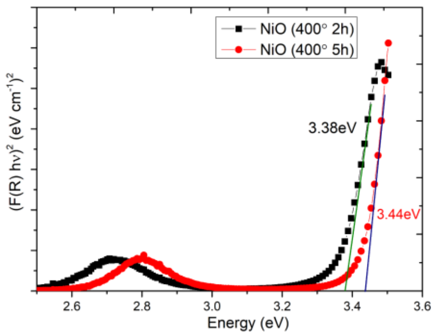


Fig.3- Tauc plots for sol–gel derived NiO films annealed at 400 °C for 2h and 5h.

NiO films with Ag electrodes exhibited higher ON-state current levels and better switching stability compared to devices using In electrodes. The improved performance in Ag-based devices is attributed to the higher mobility of Ag ions, which facilitates the formation and rupture of conductive filaments more efficiently. Moreover, films annealed for 5 hours demonstrated superior memristive characteristics, including larger memory windows, lower switching voltages, and improved endurance. This can be attributed to enhanced crystallinity and reduced structural defects, which enable more stable and reproducible filament formation during resistive switching cycles.

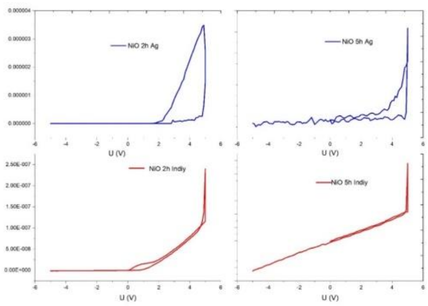


Fig.3- (I–V) comparison of NiO films with In and Ag electrodes after annealing, highlighting switching behavior.

Conclusion. In this study, NiO thin films were successfully synthesized via the sol–gel spin-coating method, and the effects of post-annealing time and electrode material on their structural, optical, and memristive properties were systematically investigated. XRD analysis confirmed the formation of polycrystalline NiO with enhanced crystallinity and grain growth for films annealed for 5 hours. Optical characterization revealed that prolonged annealing slightly increased the optical bandgap, suggesting reduced defect densities and improved structural ordering.

Memristive devices fabricated with Ag and In electrodes exhibited typical bipolar resistive switching behavior. Devices with Ag electrodes demonstrated superior switching stability and higher ON-state currents compared to those with In electrodes. Moreover, films annealed for longer durations exhibited enhanced memristive performance, including larger memory windows, better endurance, and more stable filament formation.

These results highlight the critical role of post-annealing treatment and electrode engineering in tailoring the performance of NiO-based memristive devices. Precise optimization of thermal processing conditions and electrode material selection can significantly enhance device reliability and functionality, offering valuable insights for the future development of high-performance resistive switching memories and neuromorphic computing applications.

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