Interface-Driven Thermoelectric Switching Performance of VO$^+$-Diffused Soda-Lime Glass

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1. Introduction

Vanadium oxide is one of the most promising and deeply studied materials in smart and energy materials applications. Recently, the thermoelectric behavior of vanadium oxides has been recognized as highly attractive concerning meeting energy efficiency requirements. Recent reports on the Seebeck coefficient of a vanadium pentoxide (V$_2$O$_5$) thin film on silica glass ($-680 \mu$V K$^{-1}$)[1] and annealed bulk V$_2$O$_5$ ($-618 \mu$V K$^{-1}$)[2] are highly promising for the development of a V$_2$O$_5$-based thermoelectric generator. In addition, there has been an enormous focus on and wide studies of V$_2$O$_5$/VO$_2$ thin films for micro- and thin-film battery applications due to their promising higher specific capacity.[3] In the attempt to replace Li-ion batteries, current research is focused mainly on Na-ion-based solutions due to the abundant availability and low cost of sodium.[4] Thus, in addition to the studies on the Li-ion insertion and extraction mechanisms,[5,6] the Na-ion insertion and extraction mechanisms for vanadium oxide-based systems are also being investigated.[7,8] The intercalation reaction of Na into the NaVO$_x$ product layer under a chemical gradient is being intensely studied for vanadium oxide-based materials in Na-ion battery applications.[9–11]

Although vanadium pentoxide is being explored for many functional applications, its metal—insulator transition behavior is highly debated. Various investigations have reported significantly different temperatures at which this transition is observed, viz., $\approx127$ °C,[12] $260$ °C,[13] or $338$ °C.[14] Vanadium pentoxide (V$_2$O$_5$) is observed to exhibit distinguishable and unique functional properties when it is deposited on different types of substrates.[14–16] Moreover, vanadium-containing amorphous semiconducting glasses are also being extensively studied, for example, as smart functioning glass.[17] However, there is no fundamental understanding of the mechanisms responsible for these exciting temperature-dependent properties of V$_2$O$_5$ or their temperature dependence. For final breakthrough commercialization, cost-effective and simple processing techniques must be developed along with an in-depth understanding of the material system for the entire temperature interval under consideration.

The present study focuses on the functional behavior of cost-effective sputter-deposited vanadium oxide thin films on a commercial glass substrate such as soda-lime glass and a detailed investigation of the temperature-dependent reversible interactions of native elements in the amorphous vanadium pentoxide/soda-lime glass system by in situ temperature-controlled time-of-flight secondary-ion mass spectrometry (ToF-SIMS). In addition, temperature-dependent conductivity measurements were carried out to understand the thermoelectric behavior of the V$_2$O$_5$/soda-lime glass.

2. Results and Discussion

Figure 1a shows the depth profile and mass spectrum (please refer Figure S1, Supporting Information) of soda-lime glass, respectively, substantiating the presence of Na$^+$ as a major...
constituent of the glass along with minor K\(^+\) and Ca\(^+\) additives. The intensities of Na\(^+\) are found to be almost constant through the sputtered glass substrate.

The vanadium oxide thin film was sputter deposited on soda-lime glass, as explained in the Experimental section. Figure 1b shows the ToF-SIMS depth profile through V\(_2\)O\(_5\) analyzed at 25 °C. The signals for VO\(^+\), Na\(^+\), NaVO\(^+\), and Si\(^+\) are shown. The ToF-SIMS spectrum also contains signals from V\(^+\) and a wide range of V\(_x\)O\(_y\)\(^+\) cluster ions in the V\(_2\)O\(_5\) layer as well as traces of K\(^+\), Ca\(^+\), and Al\(^+\) in the glass substrate. These signals are not included in Figure 1b for the sake of clarity.

The ToF-SIMS depth profile shows the presence of Na\(^+\) through the entire thickness (≈80 nm) of the thin film already in the as-deposited state. This is likely due to diffusion of Na into the amorphous vanadium oxide thin film during sputter deposition with the soda-lime glass substrate acting as a source for Na\(^+\). The surface is found to be enriched with oxygen, suggesting the presence of higher oxide states of vanadium along with minute trace amounts of Na\(^+\) as also reported by others.\(^{[18]}\) Further, the intensity of Na\(^+\) is negligible at the surface, which is also supported by X-ray photoelectron spectroscopy (XPS) analysis. Figure 2a,b shows results of XPS on a vanadium oxide thin film. The survey spectrum clearly reveals the presence of V and O species in the deposited thin films along with low levels of C and N, typical of organic contaminants commonly observed on samples that have been exposed to ambient air.\(^{[19]}\) No traces of Na were revealed on the XPS survey spectra, as shown in Figure 2a. The interface between the thin film and the glass substrate is characterized by enrichment/segregation of Na\(^+\) and the formation of NaVO\(^+\) (Figure 1b). The NaVO\(^+\) profile is roughly Gaussian shaped and an inverse Gaussian-like peak is observed for V\(^+\) at the film/substrate interface. Na\(^+\) diffusion is not expected to alter the oxidation state of V by the negative charge feedback mechanism for the transition metal oxides, as explained by Raebiger et al.\(^{[20]}\)

Figure 2b shows the core-level XPS spectrum of V and O. The binding energies of 517.3 and 530.2 eV were detected for V\(_{2p3/2}\)
and O1s, respectively, in the as-prepared thin-film V2O5/glass. The binding energy splitting between the V2p3/2 and V2p1/2 states was found to be 7.2 eV. The peak values are in good agreement with the previously reported data for stoichiometric V2O5 at room temperature within an experimental uncertainty of about ±0.1 eV. As the core level peaks of O1s and V2p1/2 are narrow and represent a single oxidation state, the peaks were not deconvoluted further to quantify minor oxidation states.

Interestingly, the ToF-SIMS depth profile showed unambiguous evidence for the occurrence of (sputtering-induced) diffusion of V⁺ and its oxides into the glass substrate. The ToF-SIMS mass spectrum of soda-lime glass (please refer Figure S1, Supporting Information) substantiates the absence of V in the substrate prior to the film deposition. Hence, diffusion of V⁺ into the glass and the formation of NaVO⁺ near/at the interface occur either during or after the sputter deposition of the V2O5 thin film.

Diffusion of Na⁺ from silica-based glass into a vanadium oxide thin film has been reported previously. In contrast, soda-lime glass as a substrate for VO2 coating was very rarely utilized. It was found to be highly challenging to optimize the coating procedure for thermochromic applications. However, to the best of our knowledge, there are no reports available demonstrating segregation formation of NaVO⁺ at the film/substrate interface. An order-of-magnitude estimate of the sputter-induced diffusion coefficient of Na⁺ in silica suggests a value of about 3 × 10⁻²⁰ m² s⁻¹, which would correspond to the value predicted for Na diffusion in SiO₂ at 115 or 10⁷ °C according to the tracer measurements of Frischat or Tanguerp Njiokep and Mehrer respectively. The estimated effective temperatures are found to be much lower than the experimentally predicted activation temperature, i.e., less than 200 °C required to initiate Na diffusion into the thin film.

To investigate the reversible semiconductor-to-metal transition (SMT) behavior of amorphous V2O5, the thin-film system was heat-treated in the temperature range of 25–340 °C and the ToF-SIMS analysis was (concurrently) conducted in situ.

![Figure 3](image-url)

*Figure 3.* In situ-temperature based ToF-SIMS depth profiles cycles of V2O5/glass. Time sequence shown by arrows starting from 300 to 340 °C and subsequent cooling cycle followed by cycles 2 and 3.
For the soda-lime glass, the ToF-SIMS profile obtained at 300 °C showed no change of the element intensities except a minor depletion of Na⁺ near the surface (please refer Figure S2, Supporting Information).

The complete set of the depth profiles of V₂O₅/glass is shown in Figure 3 for all temperatures under investigation. Strikingly, NaVO⁺ appeared prominently at 300 °C in the vanadium-diffused glass and the intensity of the NaVO⁺ signal remained constant up to 340 °C.

In Figure 4, the ToF-SIMS depth profiles recorded for VO⁺, Na⁺, and NaVO⁺ during thermal cycling are shown for two limiting temperatures of 25 and 340 °C. An enrichment of Na⁺ ions is prominent at the V₂O₅/glass interface at temperatures above 300 °C, as shown in Figure 3. During heating, the intensity of V and its oxides is seen to increase, their distribution is flattened out, and the sputter-induced “gap” at the interface disappears upon heating to 340 °C. The intensity of the NaVO⁺ signal is also reduced at the interface at 340 °C, as shown in Figure 4c, and it appears again when the temperature is decreased to 25 °C. Simultaneously, an interface-related gap in the VO⁺ distribution is formed when the temperature is lowered below 300 °C.

Figure 3 shows a systematic and reversible evolution of the Na⁺, NaVO⁺, and VO⁺ signals. Remarkably, the initial (as-sputtered) intensity levels are retained upon cooling to 25 °C. At the same time, the NaVO⁺ interface and the substrate-related peaks disappear. The sample was cycled three times between 25 and 340 °C to ensure the reversibility of the aforementioned reactions shown in Figure 4a–c.

Figure 5 shows the 3D maps corresponding to the distributions of VO⁺, Na⁺, and NaVO⁺ at 25 and 340 °C. It is evident that the expected reaction Na + VO ⇔ NaVO occurs uniformly in planes parallel to the film/substrate interface for the whole ToF-SIMS sputtered area of 100 × 100 μm².

Figure 6a,b shows the switching behavior (complete reversibility) of the relative intensity of NaVO⁺ with respect to the total intensities of VO⁺ and Na⁺ during all thermal cycles. This revealed that the major changes occurred at the interface and in the substrate but not at the surface of the thin film. In other words, the stable surface oxide state of V₂O₅ helped
as a protective/passivation layer obstructing secondary reactions. The observed reactions are reproducible and unambiguous as all thermal cycles for the in situ ToF-SIMS experiments were conducted under high vacuum conditions.

Figure 7a,b shows the first and third cycles of the conductivity measurements as a function of both frequency and temperature of the V$_2$O$_5$/soda-lime glass, respectively. The initial surface conductivity level of as-deposited amorphous V$_2$O$_5$/soda-lime glass is much lower (8.23 × 10$^{-10}$ S cm$^{-1}$). As shown in Figure 7a, the low-frequency response of the conductivity substantiates that the initial stabilization of the thin-film/glass system that occurred below 200 °C. The stabilization might be due to the dissociation of adsorbed oxides and water molecules from the surface of the thin film. After the stabilization of the initial reactions, the conductivity varies reproducibly between the values of 25 and 340 °C, respectively, for all subsequent cycles. The experimental behavior is well matched with the literature reports for the bulk vanadium-based semiconducting glass system, except for the particular features of the high-frequency (≈5 KHz to 2 MHz) response.

Figure 5. a–f) 3D maps of the distributions of VO$^+$, Na$^+$, and NaVO$^+$ at 25 °C (a–c) and 340 °C (d–f), respectively.

Figure 6. a,b) Relative intensity ratios of NaVO$^+$/VO$^+$ (a) and NaVO$^+$/Na$^+$ (b) comparing three subsequent temperature cycles between 25 and 340 °C.
Gradual and reversible changes of the response between 300 and 340 °C at these frequencies are observed. The formation of NaVO⁺ is prominent just at 300 °C and its fraction remains constant in the glass, which supports the assumption of linear ac conductivity behavior of the glass system. Hence, in the present case, the observed changes in the dielectric component of the V₂O₅/soda-lime glass strongly correlate with the reversible, segregation-induced interfacial production/decomposition of NaVOₓ alone.

3. Advanced Functionalities

Three unique temperature-dependent reaction mechanisms are found in the V₂O₅/soda-lime glass system.

3.1. Change of Electrical Conductivity of the V₂O₅/Glass System

In the present study, the temperature-dependent conductivity increments (Figure 7a,b) and the ToF-SIMS results elucidating reversible temperature-dependent solid-state reactions in the V₂O₅ thin-film/soda-lime glass provide evidence of the possibility for the fabrication of a thermoelectric generator[17,30] or smart window applications.[31] Further, here, it is important to emphasize that the investigated V₂O₅/soda-lime glass system displays at least 80% optical transparency in the visible spectral region with an optical bandgap of 2.3 eV. This property combination is highly beneficial for the fabrication of transparent thin-film-based thermoelectric generators and thermal sensor devices.

3.2. Formation of NaVO⁺ in the Glass Matrix

Vanadium, with its stabilized oxide and ionic states, diffused into the glass matrix in the presence of Na⁺. During heating, Na⁺ and VO⁺ combined and formed NaVO⁺ (Figure 5 and 6c). Ultimately, the reaction of Na + VO = NaVO is expected to produce excess electrons. Upon cooling, the NaVO⁺ separated into ionic states of Na⁺ and VO⁺, which is already demonstrated as stored charge concentration in the dielectric glass medium. The current study verifies charging and discharging mechanisms by solid-state reactions upon thermal cycling. Hence, the current results indicate that the produced electricity from the thermal behavior of vanadium oxides can be stored directly into the soda-lime glass.

3.3. Thermal Response of the Confined Ionic Interface Layer

The systematic alterations of ionic states (VO and NaVO complex) by segregation shown by in situ ToF-SIMS (Figure 3) were well correlated with the concurrently recorded higher-frequency response of electrical conductivity (Figure 7). As we expect the NaVO⁺ nanointerface to outperform with conventional thin film-based devices regarding the electrical conductivity and optical response, we propose a conceptual design of a “thermodynamically confined ionic interface/segregation layer” to serve as a thermoelectrical/thermo-optical switch or sensor.

4. Conclusion

The present work primarily focused on the meticulous characterization of a vanadium oxide thin film coated on commercial glass to reveal its smart functional behavior. The observed results substantiate the formation of a thermodynamically confined ionic interface. The diffused vanadium in the glass was introduced by a simple sputter deposition process. Furthermore, the thermal behavior of the thin-film/glass system is highly reversible and stable. Recent in situ TEM work[32] illustrates that no bulk transitions, such as an oxidation state change or the crystallization of the amorphous vanadium pentoxide thin film, occur below 400 °C. Permanent vanadium oxidation state intensity changes were not observed in the depth profiles obtained by ToF-SIMS.
For the first time, the production of interface-confined NaVO$^+$ via a solid-state thermal reaction of vanadium pentoxide with sodium ions supplied by the soda-lime glass substrate is documented. The observed temperature-dependent conductivity increments commonly reported for vanadium oxide-based and vanadium-containing glass could be explained by thermal activation in semiconducting glasses.\textsuperscript{[26–29]} However, these results provide evidence for metal–metal interactions of vanadium oxide during SMT, which induced the conjugation of VO$^+$ with Na$^+$ to form NaVO$^+$ in the glass.

Characterization of this V$_2$O$_5$/soda-lime glass remains challenging and opens new research directions as prospects for future work. 1) Depth-dependent oxidation state and valence state determination of vanadium, 2) diffusion kinetics of vanadium in the complex glass in the presence of Na$^+$, 3) interface formation mechanism by different processing methods and conditions and the actual conditions responsible for the observed thermal behavior of the interface, 4) the importance of soda-lime glass for the formation of NaVO, 5) determination of electrical and optical constants of individual layer systems (thin film, interface, and V$^-$-diffused glass) as a function of temperature, and 6) designing electrical components of V$_2$O$_5$/soda-lime glass.

In conclusion, the present study demonstrates the potential of V$_2$O$_5$ thin films for a self-chargeable transparent thin-film thermoelectric generator on a commercial window glass and many more applications, which can be realized in the near future. The obtained results of vanadium diffusion in the glass show new perspectives concerning the basic understanding of the thermal response of vanadium oxide-based semiconducting glass bulk systems.

5. Experimental Section

Thin films of V$_2$O$_5$ were deposited on glass substrates (Thermo Fisher Scientific Silica-based microscope slides) using a vanadium metal target (99.95% purity) with a room temperature reactive sputtering process. The DC Magnetron sputtering instrument (BesTech) was operated at a power of 40 W for the current study. The vacuum chamber was pre-evacuated to a pressure $<7.5 \times 10^{-4}$ mbar and the working pressure was adjusted to $5 \times 10^{-3}$ mbar with an O-to-Ar ratio of (2:3) in terms of partial pressures. The thicknesses of the V$_2$O$_5$ thin films were measured by a surface profilometer (Bruker DektakXT). The thicknesses were averaged over a minimum of five measurements on at least two similarly processed samples to $\approx$80 nm.

The ToF-SIMS depth profiles were measured using a custom instrument, which was largely equivalent to the IONTOF M6. The spectrometer was run at an operating pressure of $<10^{-4}$ mbar. The depth profiles were measured in a dual-beam mode, using a 30 keV Bi$^{+}$ primary ion source with a pulsed current of 0.02 pA for analysis and a 1 keV Ar source with a current of 200 nA for sputtering. Analysis was conducted over a 100 $\times$ 100 mm$^2$ area and sputtering was conducted over a 500 $\times$ 500 mm$^2$ area. The sputtering depth was calibrated via the known film thickness and assuming a constant sputtering rate. As we are not quantifying any diffusion properties of the elements, this approximation is suitable for the present purposes. The depth profiles are shown as dead-time-corrected absolute intensities without normalization and averaged over the analyzed area, assuming a lateral homogeneity of the samples over the entire area of the thin film on the glass substrate.

An Axis-Ultra spectrometer (Kratos, Manchester, UK) with charge neutralizer was used to obtain X-ray photoelectron spectra with monochromatic Al K$_x$ radiation ($h\nu = 1486.6$ eV). Acceleration voltage and emission were set as 12 kV and 10 mA, respectively. An impedance spectrometer (Agilent 4192A LF impedance analyzer) was used to analyze the AC conductivity changes of the thin film in the temperature range 25–340°C. For this reason, spring-loaded Au contacts were configured and tested. The frequency range from 5 Hz to 2 MHz was utilized with multiple intervals. The AC voltage was set to 1.0 V for all measurements.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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