Electrostatic Tuning of Ionic Charge in SiO$_2$ Dielectric Thin Films

Isabel Al-Dhahir, Rachel Kealy, Samira Kelly, Mingzhe Yu, Shona McNab, Katherine Collett, Junliang Liu, Chris Grovenor, Peter R Wilshaw, and Ruy Sebastian Bonilla*

Department of Materials, University of Oxford, Oxford, OX1 3PH, United Kingdom

*E-mail: sebastian.bonilla@materials.ox.ac.uk

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Abstract: Dielectric thin films are a fundamental part of solid-state devices providing the means for advanced structures and enhanced operation. Charged dielectrics are a particular kind in which embedded charge is used to create a static electric field which can add functionality and improve the performance of adjacent electronic materials. To date, the charge concentration has been limited to intrinsic defects present after dielectric synthesis, unstable corona charging, or complex implantation processes. While such charging mechanisms have been exploited in silicon surface passivation and energy harvesters, an alternative is presented here. Solid-state cations are migrated into SiO$_2$ thin films using a gateless and implantation-free ion injecting method, which can provide greater long-term durability and enable fine charge tailoring. We demonstrate the migration kinetics and the stability of potassium, rubidium, and caesium cations inside of SiO$_2$ thin films, showing that the ion concentration within the film can be tuned, leading to charge densities between 0.1-10 x 10$^{12}$ qcm$^{-2}$. A comprehensive model of ion injection and transport is presented along a detailed investigation of the kinetics of alkali cations. Integrating ionic charge into dielectrics to produce controlled electric fields can enable new architectures where field effect is exploited for improved electron devices.

1. Introduction

Ion-charged dielectrics (ICDs) are a class of thin film electret materials that holds a quasi-permanent charge. The charge storage capability of electrets makes them effective for a wide range of applications. From telecommunications to air filters and biomedical instruments, charged dielectrics are useful for a variety of devices where high charge density films with stable polarisation are required. Various dielectrics common to the electronics industry have already been shown to possess an intrinsic concentration of fixed charge ($Q_f$) readily available after film synthesis. This includes for example silicon oxide (SiO$_2$), silicon nitride (SiN$_x$) and aluminium oxide (AlO$_x$). It is noted here that the term intrinsic is used here to refer to the concentration of charge obtained directly after synthesis of the dielectric thin film. This is opposed to other charge concentration that can be added extrinsically using further processing. Typically, the intrinsic $Q_f$ is of low to moderate value, and thus it does not contribute significantly to the electret's electric field since it is limited by the dielectric synthesis process. Supplementary methods to produce substantial charge have been developed to fully exploit the electret potential of such films. These methods are used after dielectric synthesis and therefore are termed “extrinsic”. For example, extrinsic charge can be introduced to a dielectric through corona charging, electron beam, ion implantation or alkali ion migration. While most of these techniques result in charge that is stable for a few weeks at most, alkali ions have been recently reported to be stable for years. Potassium ions ($K^+$), for example, have been incorporated into a SiO$_2$ thin film and shown to withstand laboratory conditions for at least 4 years. New explorations of this concept include recent reports of Sr$^{2+}$ and Al$^{3+}$ ions inside SiO$_2$ matrices, as well as the use of potassium charged AlO$_x$ for neuromorphic computing, or transition metal oxides as the base material for novel electrets. Within the field of transparent conductors, K$^+$ doped graphene has also been
recently demonstrated to increase carrier mobility. This new range of application for ICDs calls for an in-depth investigation on methods to produce and tailor such materials.

To the author’s knowledge, the first report of ICDs was the work of Yamin in 1965. Yamin examined the diffusion of ions across SiO$_2$ in metal-oxide-semiconductor (MOS) structures and their response to a surface potential at elevated temperatures. These ions were found to be sodium (Na$^+$) contaminants and were determined to be a key source of instability in silicon devices due to their high mobility even at low temperatures. In further studies, the larger K$^+$ ion was also shown to respond to surface potentials, however, with stronger charge trapping at the Si-SiO$_2$ interface. As a result, K$^+$ exhibited greater stability than Na$^+$. Nauta and Hillen explained the behavioural difference in the two ions by studying their activation energies. They showed that under a bias of +2.5 V and temperatures ranging between 50 - 350 °C, the activation energy of Na$^+$ and K$^+$ ions at an Al-SiO$_2$ interface was 1.10 eV and 1.65 eV, respectively. Under the same thermal stress and equivalent reverse bias, the activation energy of the ions trapped at the Si-SiO$_2$ interface was reported to be 1.01 eV and 1.65 eV, respectively. The higher activation energy of K$^+$ ions at both interfaces in comparison to that of Na$^+$ ions lowers the probability of de-trapping, which improves the stability of the ions inside of the thin film. Recent work has shown that K$^+$ ions remain quenched at the Si-SiO$_2$ interface for up to 8 years held at a temperature of 65 °C under vacuum. Additionally, while corona or electron beam charge injection works well on planar surfaces, methods of K$^+$ introduction are more compatible with confined or trenched device components due to their versatility. In view of these advantages, K$^+$ ion embedding has emerged as a promising method of establishing durable electric fields and thus functionalise dielectric materials.

Potassium ion electrets have been used in a range of applications. Recently, they have been reported in vibrational energy harvesters, pressure sensors and actuators. In the field of electrostatic energy harvesters, the use of such electrets has produced force factors on the order of $10^4$ to $10^5$ C m$^{-1}$. Owing to such high force factors, power conversion efficiencies of 80.7 % have been achieved. Potassium ion electrets have also been applied to silicon surface passivation for photovoltaics (PV). The charge residing in such dielectrics is reported to provide effective passivation by minimising the concentration of one type of charge carrier at the silicon-dielectric interface and thus reducing the recombination rate. This is known as field effect passivation (FEP). Surface passivation studies of SiO$_2$ electrets embedded with K$^+$ ions on 1 Ω cm float zone n-type silicon have shown that surface recombination velocities (SRV) as low as 3.3 cm s$^{-1}$ can be achieved compared with SRV ~100 cm s$^{-1}$ of SiO$_2$ alone. For such high performance passivation to be practical in commercial manufacturing it must be durable for ~30 years under field conditions, as this is the approximate lifespan of a solar cell. Ageing studies conducted on K$^+$ embedded electrets have so far only concentrated on laboratory conditions and have shown that 63 % of the initial passivation performance is retained after a projected 45 years. Additionally, evidence of potential induced degradation in PV modules has been largely attributed to the diffusion of sodium ions in response to operational voltages. It is plausible that larger alkali ions may permit similarly high charge density dielectrics with improved durability due to their increased size within the amorphous oxide matrix. In this paper we will focus on the methods of tuning ionic charge concentration and its stability within the dielectric. In a subsequent work we will explore their surface passivation potential.

Other authors have asserted that alkali ions larger than K$^+$ are unlikely to migrate across an oxide film. In this manuscript, we demonstrate that it is in fact possible to migrate large alkali ions trough a SiO$_2$ thin film. Potassium, rubidium (Rb$^+$), and caesium (Cs$^+$) cations are all shown to respond to a surface electric field, inject into the oxide matrix at high temperature, and provide an interface electric field. The methodology by which such alkali cation
concentration can be established is explored here in detail, and the presence of all three ions within the oxide is confirmed using Secondary Ion Mass Spectroscopy (SIMS). To understand the kinetic process, a model of ion injection into the oxide and transport to the Si-SiO₂ interface is developed. Contrary to prior work, this model accounts fully for both injection and migration processes, while also considering the electrostatic interaction of ions in the presence of a variable electric field. The kinetics and stability of Rb⁺ and Cs⁺ ions in SiO₂ are studied experimentally and used to find the kinetic parameters via the proposed model. The previously reported work on K⁺ ions is also revised here using the updated model, as well as providing an analysis of ion stability.

2. Physical Model of Ion Injection, Transport and Trapping

A model of ion injection at the surface and transport through the dielectric is first presented here. Due to its relevance and ubiquity in electronic devices, the model has been optimized for the case of alkali ionic charge in a SiO₂ thin film. The model uses finite element analysis to simulate ion migration into and across the thin film. Here, a SiO₂ film of thickness \( d \) is discretised into \( n \) number of equal elements. As SiO₂ is known to possess a small native concentration of positive charge, \( 12 \), a concentration of \( 8 \times 10^{15} \) q cm\(^{-3} \) was assumed to exist uniformly within each element prior to the introduction of extrinsic charge. This is equivalent to an effective interface charge concentration of \( 4 \times 10^{10} \) q cm\(^{-2} \), which has been corroborated using capacitance-voltage measurements, as described in Section 3.

A schematic diagram of the air-oxide-silicon system is depicted in Figure 1. On the surface of the dielectric, the ions are bound to Cl⁻ since a chloride salt is used as a precursor here. In a bound state, the alkali ions face a considerable energy barrier to enter the SiO₂. The energy required to overcome the barrier at the air-oxide interface is referred to as the activation energy of injection (\( \Delta E_{ao} \)). The distribution of activation energies has previously been approximated most typically using either single energy values, \( 48 \) or Gaussian distributions, \( 32, 49-51 \). In this work a single activation energy is used for simplicity. Ions are thermally excited over the injection barrier during a high temperature anneal. Upon injection into the SiO₂, the ions exist in a free state and contribute to the positive charge within the SiO₂. As the concentration of ions within the SiO₂ increases, negative mirror charge accumulates at the Si surface resulting in an electric field. This field can be further augmented by the presence of positive corona charges on the SiO₂ surface. The field provided by corona charges is not stable throughout the anneal and decays with time and increasing temperature, \( 18, 52 \). The effect of the corona charge concentration over various annealing times and temperatures hence requires investigation in order to construct an appropriate model. The ions arriving at the Si-SiO₂ interface are assumed to be similarly trapped at a single energy level, \( \Delta E_{os} \). The accumulation of ions at the Si-SiO₂ interface generates a field that reduces the corona-induced field, and thus limits further ionic migration.
2.1. Ion Injection at the Air-\(\text{SiO}_2\) and Trapping at the Si-\(\text{SiO}_2\) Interfaces

The rate determining step of ion migration is the de-trapping and trapping of ions at the air-oxide and oxide-silicon interfaces, respectively. Since these rates are directly proportional to the concentration of ions, either trapped at interfaces or de-trapped in the oxide bulk, a first-order kinetic approach is used to model ion injection at the air-oxide interface and ion trapping at the oxide-silicon interface.

Firstly, the concentration of ions trapped at the \(\text{SiO}_2\) surface (\(C_{\text{ao}}\)) is calculated using Equation 1:

\[
\frac{dC_{\text{ao}}}{dt} = C_1 \times N_{\text{trap}}(E,t)R_{\text{trap}}(E) - C_{\text{ao}}(E,t) \times s \times e^{-\frac{\Delta E_{\text{ao}}}{kT}}
\]

where the first term in the RHS represents increases in ion concentration due to trapping and the second term represents decreases in concentration due to injection into the \(\text{SiO}_2\), mediated by an energy barrier. As ions are released into the oxide, the number of trap states available at the air-oxide interface increases. The total number of trap states is set to \(10^{13}\) cm\(^{-2}\) following references 49 and 53, and the capture rate (\(R_{\text{trap}}\)) set to \(10^{11}\) cm\(^{-2}\) s\(^{-1}\). The ion concentration within the first segment of the oxide film (\(C_1\)) therefore has a re-trapping probability at the \(\text{SiO}_2\) surface equal to \(N_{\text{trap}}(E,t)R_{\text{trap}}(E)\). The escape frequency (\(s\)) defines the dynamics of ion release. Following reference 49, a value of \(5 \times 10^{11}\) s\(^{-1}\) was used for \(s\), while the activation energy of the barrier is left as a fitting parameter.

Ion trapping at the Si-\(\text{SiO}_2\) interface is expressed similarly in Equation 2. Here, \(C_n\) is the concentration of ions in the last element of the \(\text{SiO}_2\). It is assumed there is no trapped charge at the interface at time \(t = 0\).
\[
\frac{dC_{os}}{dt} = C_r \times N_{trap}(E,t)R_{trap}(E) - C_{os}(E,t) \times s \times e^{-\frac{\Delta E_{os}}{kT}}
\]  

(2)

The effective interface charge concentration \(Q_{eff}\) at the Si-SiO\(_2\) interface at time \(t\) is calculated as a function of the ionic concentration \(C_x\) at position \(x\), following Equation 3.

\[
Q_{eff}(t) = q_e \sum_{x=d}^{\infty} C_x \times \frac{x}{d}
\]

(3)

\(Q_{eff}\) represents the measurable ionic charge when using, for example, capacitance-voltage technique,\(^{54}\) and assuming that the charge centroid lies at the oxide-silicon interface such that \(x = d\). This is chosen due to the use of capacitance-voltage characterisation as further described in Section 3.

### 2.2. Ion Transport Through SiO\(_2\)

The SiO\(_2\) matrix allows ions to diffuse through large interstitial sites created by the continuous interconnected network of tetrahedral SiO\(_4\) molecules.\(^{55,56}\) The energy required to allow ion transport through the dielectric is called the diffusion activation energy, \(\Delta E_d\). The Anderson-Stuart model of diffusion defines \(\Delta E_d\) as the sum of the electrostatic binding energy of the ion and the strain energy required to dilate the oxide structure to permit movement of the ion.\(^{57}\) The model delivers a parabolic dependence of activation energy on ionic radius. Despite inducing minimal distortion of the oxide, ions of a smaller ionic radius than Na\(^+\) have a high \(\Delta E_d\) due to their greater binding force to O\(^-\) ions of the oxide. On the other hand, ions larger than Na\(^+\) possess a smaller binding force but have increasingly higher \(\Delta E_d\) caused by greater network strain energy. The mobility \((\mu)\) of the ions through the dielectric as a function of temperature is defined as:

\[
\mu = \mu_0 e^{-\frac{\Delta E_d}{kT}}
\]

(4)

Table 1 lists a range of mobility pre-factors \((\mu_0)\) that have been reported in the literature for K\(^+\) ions within SiO\(_2\). These values differ by up to 1 order of magnitude. Previously reported mobility data of K\(^+\) ions within SiO\(_2\) is plotted in Figure 2. Stagg’s results were determined from transient ion current (TSIC) measurements performed on MOS structures between 227-297 °C.\(^{58}\) Hillen et al. used triangular voltage sweep (TVS) measurements between the temperature range 300-450°C, and found very close correspondence to Stagg’s data.\(^{59}\) Hillen et al. additionally determined an expression for \(\mu_0\) as function of temperature (provided in Table 1) and found that within the temperature range studied, \(\mu_0\) has negligible influence. Greeuw and Verwey similarly used TVS measurements, however, their results do not correlate well with the other authors’.\(^{46}\) No explanation is given for the discrepancy in results, however, it is reported that \(\mu_0\) could vary depending on oxidation conditions and temperature.\(^{46,59}\) Despite the discrepancy in \(\mu_0\), the corresponding values of \(\Delta E_d\) given in Table 1 are in excellent agreement with each other. Given such uncertainty in \(\mu_0\), it was adjusted in this work as a fitting parameter to ensure the value of \(\Delta E_d\) is in good agreement with the literature. Here \(\mu_0\) was set to 0.05 cm\(^2\)V\(^{-1}\)s\(^{-1}\), which is within the range calculated by Stagg and just outside the range calculated by Hillen et al.\(^{59}\) To the author’s knowledge, no data exist for Rb\(^+\) and Cs\(^+\) ions therefore this pre-factor was kept constant for all three ions.
Following the Einstein relation, the diffusivity can be calculated as:

\[ D = \frac{kT \mu}{q_e} \]  \hspace{1cm} (5)

where \( q_e \) is the elementary charge. The migration of ions across the dielectric is governed by Fick’s laws of diffusion. At elevated temperatures, alkali ions injected into the SiO\(_2\) are driven across the film with the driving force provided by the concentration gradient. The concentration gradient is supplemented by an external surface bias and the Coulombic attraction between the ions and the mirror charges that appear at the Si surface. The total flux within the system is therefore the sum of the diffusive flux and the drift flux. Following Fick’s first law, the diffusive flux is given as:

\[ J_{\text{diff}} = -D \frac{dc}{dx} \]  \hspace{1cm} (6)
where $C$ is the ionic concentration per unit volume. The flux arising from drift is expressed as:

$$J_{\text{drift}} = \mu e C$$  \hspace{1cm} (7)

where $\varepsilon$ is the electric field present within each element.

There are three sources of electric field. The first is the field from surface corona charges ($\varepsilon_{\text{corona}}$), purposefully applied to enhance migration. This electric field source is not constant as the instability of corona charge increases with temperature. Experimental data recording the decay of surface charge over time was taken in 50 °C increments between 200 °C and 500 °C and included in the supplementary materials. The field from the corona charge experienced in every element of the SiO$_2$ is reduced by the amount of injected ionic charge. This is since Cl$^-$ anions left behind after K$^+$ injection effectively neutralise the corona surface charge. Consequently, the field experienced within each element as a function of time is calculated from Gauss' Law as:

$$\varepsilon_{\text{corona}} = \frac{q_e C_{\text{corona}}(t) - q_e \sum_{x=d}^{d} C(x,t)}{\varepsilon_{\text{ox}} \varepsilon_0}$$  \hspace{1cm} (8)

where $C_{\text{corona}}$ is the surface concentration of corona charge per unit area.

The second contribution to the electric field arises from the ionic charge within each element ($\varepsilon_{\text{ions}}$). The overall electric field is the sum of all the field contributions at position $x$, with greater contribution the closer to the oxide-silicon interface since more ions reside there. Therefore, we calculate the field within each element at time $t$ by performing a cumulative integration at time $t$ with respect to position $x$ as:

$$\varepsilon_{\text{ions}} = \int_0^{x=d} C_{\text{ions}}(x,t) \times q_e \frac{\varepsilon_{\text{ox}} \varepsilon_0}{dx}$$  \hspace{1cm} (9)

The third contribution is from ions that are re-trapped at the SiO$_2$ surface, which is to say ions that are ejected to the air-oxide interface. Before injection, ions are assumed to be bound to Cl$^-$ and therefore not contribute to the electric field. After injection into the SiO$_2$, the K$^+$, Rb$^+$ and Cs$^+$ are free ions that contribute to the electric field. Re-trapped ions therefore contribute to the electric field similar to any remaining corona ions, as follows:

$$\varepsilon_{\text{retrapped,ao}} = \frac{C_{\text{retrapped,ao}} \times q_e}{\varepsilon_{\text{ox}} \varepsilon_0}$$  \hspace{1cm} (10)

3. Methods and Characterisation

Silicon wafers were used in this work as the substrate for dielectric thin film growth and deposition. These were n-type 1 Ω cm float-zone, <100>, 4 inch, 200 μm thick, and were thermally oxidised to 100 nm thickness on both sides at 1050 °C in oxygen and dichloroethylene at Fraunhofer ISE. The methods of alkali ion introduction used in this work have been adapted from reference 19. Ions were deposited directly onto the oxide surface by either spin coating or thermal evaporation. For spin coating alkali ion chloride salt solutions were prepared in 25 % deionised (DI) water, 75 % isopropanol (IPA). While all these salts used present excellent solubility in water, IPA is added as it improves the wettability of the dielectric, uniformity, and evaporates quickly at room temperature. For thermal evaporation, 100 % DI water was used. Only K$^+$ ions were deposited via thermal evaporation to avoid contamination of the chamber with Rb$^+$ and Cs$^+$ ions. The purpose of using spin coating was to show versatility in the deposition method.
Figure 3. Flow chart of experimental process

A flow chart of the subsequent processing sequence is shown in Figure 3. Ion migration was assisted by a positive surface field created by corona discharge and a hotplate anneal ranging between 250 – 600 °C. Annealing is required to provide enough energy to overcome the barrier for ion injection while the positive surface field drifts the ions across the oxide. These methods follow on from those described in reference 18. Corona discharge was deposited on both sides of the specimen from a pin held 20 cm above the sample at +30 kV. The surface charge concentration was determined from Kelvin Probe measurements using a KP020 kit by KP Technologies and the analysis methods explained in reference 54. Following annealing, interface electrical characterisation was carried out through capacitance-voltage (C-V) measurements using a Keysight 4980A LCR meter. The accumulation regime was calculated using the McNutt-Sah method60 with the extension in reference 61. The interface charge was determined from the flat-band voltage $V_{fb}$ at which the semiconductor flat-band capacitance occurs.62 $V_{fb}$ is related to the volumetric ionic concentration as a function of position ($\rho(x)$) following Equation 11:

$$V_{fb} = \frac{\Phi_{ms}}{q_e} - \frac{q_e C_{it} d}{\varepsilon_i} - \frac{1}{\varepsilon_i} \int_0^d \rho(x) \, dx$$

where $\Phi_{ms}$ is the work function difference between the metal and silicon and $C_{it}$ is the interface trap charge concentration under flat-band conditions. $C_{it}$ is often considered negligible with a low concentration of $\sim 10^{10}$ q cm$^{-2}$.63 Since it is not possible to know the exact distribution of charge within the film, it is simpler to represent it as an effective sheet of charge with its centroid ($x_c$) at position $x = d$. This is termed the effective interface charge concentration $Q_{eff}$. Therefore $\rho(x)$ can be expressed as a delta Dirac function $\rho(x) = Q_{eff} \delta(x - [d - x_c])$. The flat-band voltage can then be expressed as:
\[ V_{fb} = \frac{\varphi_{ms}}{q_e} - \frac{q_e c_i d}{\varepsilon_i} - \frac{Q_{eff}(d-x_c)}{\varepsilon_i} \]  (12)

Once \( V_{fb} \) has been calculated from the C-V measurement, \( Q_{eff} \) can be determined as:

\[ Q_{eff} = \frac{\varepsilon_i}{d-x_c} \left( \frac{\varphi_{ms}}{q_e} - V_{fb} - \frac{q_e c_i d}{\varepsilon_i} \right) \]  (13)

From Equation 13, the closer the position of the charge to the Si-SiO\(_2\) interface, the more sensitive the C-V measurement. Prior to C-V measurements, metal-oxide-semiconductor (MOS) structures were prepared by etching the rear dielectric with hydrofluoric acid prior to thermally evaporating ~100 nm of aluminium in an Edwards 306 evaporator. Front contacts 1 mm in diameter were made by evaporating aluminium through a shadow contact mask directly onto the SiO\(_2\). On a subset of samples, an investigation of interface degradation was performed. Heat ageing studies were carried out in a box furnace at 120 °C for a total of 500 hours. The prepared MOS structures allowed for intermittent C-V measurements to determine the stability of the interface charge concentration. Separate samples were exposed to ultraviolet (UV) radiation at room temperature also for a total of 500 hours. An in-house UV exposure chamber was constructed using four Osram UVA lamps to achieve a total optical irradiance of ~5 mW cm\(^{-2}\). The UV spectrum and configuration are provided in the supporting information. As UV radiation cannot pass through the aluminium dots on the surface, each time the samples were removed for testing, new dots were thermally evaporated next to the previous ones. Control specimens were produced that underwent the same processing with the omission of ion deposition.

Secondary Ion Mass Spectroscopy (SIMS) was used to confirm the presence of K\(^+\), Rb\(^+\) and Cs\(^+\) ions within SiO\(_2\). Here a Thermo Scientific Helios G4 Plasma FIB DualBeam (PFIB) system combined with a Hiden Analytical EQS quadrupole SIMS detector was used. An area of 50 µm x 50 µm (100 x 100 pixels) was scanned using a focused beam of Xe\(^+\) at 5 kV and 100 pA. Selected secondary ions were collected by the quadrupole detector. This scanning process was repeated throughout the depth of the oxide film to create stacks of images showing the distribution of each element. The Hiden SIMS Mapper was then used to create elemental depth profiles.

4. Alkali Ion Dynamics in SiO\(_2\)

The effect of annealing time and temperature was studied on K\(^+\), Rb\(^+\) and Cs\(^+\) ions separately. A corona discharge time of 30 s, equivalent to a deposited surface concentration of ~2 x 10\(^{12}\) q cm\(^{-2}\), was applied to samples spin-coated with ion precursors, prior to. Figure 4 illustrates the changes in \( Q_{eff} \), measured at intervals over the course of 6 minutes annealing. K\(^+\) ions were migrated at 250 °C, 300 °C and 350 °C. The results are shown in Figure 4a. At 250 °C, a gradual increase in \( Q_{eff} \) with time was measured. A maximum \( Q_{eff} \) of ~0.8 x 10\(^{12}\) q cm\(^{-2}\) was obtained within 6 minutes of annealing. At higher temperatures of 300 °C and 350 °C the K\(^+\) ions saturated at the same \( Q_{eff} \) of ~1.8 x 10\(^{12}\) q cm\(^{-2}\), irrespective of temperature, within 60 s of annealing. In the case of Rb\(^+\) ions, a minimum temperature of 375 °C is required to detect any migration across the oxide, as shown in Figure 4b. We observe that the \( Q_{eff} \) of Rb\(^+\) gradually reaches saturation at ~1.3 x 10\(^{12}\) q cm\(^{-2}\) after 4 minutes at 450 °C. The results for the largest of the 3 ions, Cs\(^+\), are shown in Figure 4c. A minimum of 500 °C was required to detect a small amount of charge migration. After 6 minutes of annealing, \( Q_{eff} \) increases from ~4 x 10\(^{10}\) q cm\(^{-2}\) to ~2 x 10\(^{11}\) q cm\(^{-2}\). A higher temperature of 600 °C showed a more substantial increase as \( Q_{eff} \) saturates at ~1 x 10\(^{12}\) q cm\(^{-2}\) within 30 s of annealing.
Figure 4. The influence of annealing time and temperature on migrated charge at the interface at a fixed surface field for spin coated (a) K$^+$ ions (b) Rb$^+$ ions and (c) Cs$^+$ ions. Solid lines are model fittings using the parameters in Table 2.
The model described in Section 2 was used to simulate $Q_{\text{eff}}$ as a function of time and temperature for all three ions. The modelling results are represented as solid curves in Figure 4 and the parameters are provided in Table 2. Values of 1.0 eV and 1.34 eV were chosen as $\Delta E_d$ for $K^+$ and $Rb^+$, respectively. These values are in very good agreement with those proposed by Anderson, Stagg, Hillen and Greeuw.46,57–59 A value of 1.65 eV was determined as $\Delta E_d$ of $Cs^+$ ions, which is lower than the predicted value of 1.83 eV by the Anderson-Stuart model.

Table 2. Modelling parameters for the results in Figure 4

|                 | $K^+$ | $Rb^+$ | $Cs^+$ |
|-----------------|-------|--------|--------|
| $C_{ao}(t = 0)$ (x10$^{12}$ q cm$^{-2}$) | 4$^{a)}$, 10$^{b)}$ | 4 | 10 |
| $C_{os}(t = 0)$ (x10$^{12}$ q cm$^{-2}$) | 0 | 0 | 0 |
| $\Delta E_{ao}$ (eV) | 1.44 | 1.57 | 1.80 |
| $\Delta E_d$ (eV) | 1.00 | 1.34 | 1.65 |
| $\Delta E_{os}$ (eV) | 1.90 | 2.10 | 2.25 |

*a) spin coated  b) evaporated

The injection of $K^+$ ions at the SiO$_2$ surface has predominantly been studied on MOS structures and values of ~1.65 eV have been determined.18,32,46,49,58,64 In this work, ions are trapped at an air-SiO$_2$ interface. Our prior work showed that there is a significant difference in activation energy at the oxide surface depending on the presence of a metal contact.18,65 If $K^+$ ions are trapped at an Al-SiO$_2$ interface they behave differently than at an air-SiO$_2$ interface. Here, the parameter $\Delta E_{ao}$ was varied empirically to establish an accurate fitting. In the case of $K^+$, a value of 1.44 eV was determined. For $Rb^+$ and $Cs^+$ ions, activation energies of 1.57 eV and 1.80 eV were found. The parameter $\Delta E_{os}$ was similarly determined for each ion, and values of 1.90 eV, 2.10 eV and 2.25 eV were found for $K^+$, $Rb^+$ and $Cs^+$, respectively. To the author’s knowledge, no reported values of $\Delta E_{ao}$ and $\Delta E_{os}$ exist for alkali ions larger than $K^+$. Figure 5 explores the relationship between the concentration of corona charge deposited on the oxide surface and the resulting maximum $Q_{\text{eff}}$ after annealing. The relationship for $K^+$ ions is shown in Figure 5a. Samples had $K^+$ ions either spin coated or evaporated onto the surface followed by an anneal at 300 °C for 3 minutes to ensure a maximum $Q_{\text{eff}}$. A linear correlation between the corona-induced surface potential and final interface charge is evident, where the rate of ionic charge to corona charge observed at 300 °C is nearly 1. For spin coated samples where the initial ionic surface concentration is smaller, the effective interface charge saturates at ~4 x 10$^{12}$ q cm$^{-2}$, at which point the surface is presumably depleted of ions. Until this saturation point is reached, the difference in ionic surface concentration does not affect the relationship observed. Since the concentration of precursor ions is much larger for thermally evaporated KCl, the total migrated concentration continues to increase with applied surface charge. The results for $Rb^+$ ions are shown in Figure 5b. After ion deposition and corona charging, specimens were annealed for a total of 5 minutes at 450 °C. On average, a $Rb^+$ ionic charge to corona charge rate of 1/2 is observed. In the case of the larger $Cs^+$ ion, specimens were corona charged and annealed at 600 °C for 60 s. From the results in Figure 5c, it was determined that the rate of $Cs^+$ interface ions to corona charges is 2/5. These observations show that the larger the ion, the smaller the rate of injection and migration to the Si-SiO$_2$ interface, as supported by the modelling parameters obtained in Table 2.
Figure 5. The influence of surface charge concentration pre-anneal on the migrated ionic charge concentration for (a) K\textsuperscript{+} (b) Rb\textsuperscript{+} and (c) Cs\textsuperscript{+}. Solid lines are model fittings using a single value for $\Delta E_{ao}$ of 1.34 eV, 1.56 eV and 1.85 eV for K\textsuperscript{+}, Rb\textsuperscript{+} and Cs\textsuperscript{+}, respectively.
It has been previously suggested that an applied electric field may lower the energy barrier for ionic conduction through an oxide thin film.\textsuperscript{18,51,66,67} To determine if $\Delta E_{ao}$ does have a dependency of surface fields, the data in Figures 5a and 5b were modelled. Here it was determined that a single value of $\Delta E_{ao}$ could be used to model the results irrespective of surface charge concentration. Values of 1.34 eV, 1.56 eV and 1.85 eV were chosen as $\Delta E_{ao}$ for $K^+$, $Rb^+$ and $Cs^+$ ions respectively. The other parameters were the same as in Table 2. The activation energy of injection, and thus the rate of release of ions at the air-SiO$_2$ interface, is unaffected by surface field strength. The changes in the kinetics are purely given by the electrostatic components considered in our model. The weaker response of $Rb^+$ and $Cs^+$ to surface fields than $K^+$ is explained by the lower injection rate and limited drift velocity of larger ions.

The performance of electret-based devices is strongly dependent upon the charge concentration. For example, in the field of electrostatic energy harvesters, the power output is proportional to the square of the charge concentration within the dielectric.\textsuperscript{68,69} Electret devices with substantial in-built electric fields eliminate the need for DC biasing, thus benefiting from low voltage and reduced power consumption.\textsuperscript{34,70} Additionally, recent work on field-effect passivation in silicon solar cells has demonstrated that the optimal $K^+$ $Q_{eff}$ is $\geq 1.5 \times 10^{12}$ q cm$^{-2}$.\textsuperscript{71} The methodology and model presented here demonstrates that acute control of the ionic charge concentration can be achieved by tuning the processing such that it fits the device end application.

5. SIMS Profiling of Alkali Ions Within SiO$_2$

Alkali ions with a larger ionic radius than $K^+$ have long been presumed to be too big to be mobile within SiO$_2$.\textsuperscript{46} In experimental studies, Deal reported zero drift of $Cs^+$ ions in MOS structures under applied fields up to temperatures of 300 °C.\textsuperscript{47} In this paper, we show that $Rb^+$ and $Cs^+$ are indeed mobile within SiO$_2$ and are responsible for the $Q_{eff}$ recorded. To confirm this, plasma focused ion beam (PFIB) SIMS depth profiling was used to detect the presence of all three ions within the SiO$_2$ thin film. The results are shown in Figure 6. It is noted here that PFIB-SIMS has a much poorer resolution limit than other SIMS techniques which explains our preferred use of linear intensity versus cycle axes. The cycle number is an indicator of the depth into the SiO$_2$, from where atoms are being ablated. The location of the surface of the underlying Si wafer is marked by the abrupt drop in the Si$^+$ signal due to the well-known dramatic change in ion ablation yield for Si$^+$ ions at the Si-SiO$_2$ interface.\textsuperscript{72,73} Samples were prepared with KCl, RbCl or CsCl deposited on the surface followed by corona charging and annealing. Before being loaded into the PFIB-SIMS, all samples were coated with 15 nm of platinum to avoid charging from the electron beam during inspection. To ensure $Q_{eff}$ can be predominantly attributed to each of these ions, common laboratory contaminants such as Na$^+$ and $K^+$ were also profiled. In the KCl sample, Figure 6a confirms the majority presence of $K^+$ ions in the SiO$_2$ layer, and only a negligible signal intensity denotes a trace contamination by Na$^+$ ions. Figure 6b shows results from two samples where $Rb^+$ ions were introduced to the oxide by corona charging for 30 s and 180 s, respectively, followed by 5 minutes of annealing at 450 °C. The sample with the longer charging time, and therefore stronger surface electric field, shows deeper penetration of $Rb^+$ ions into the oxide layer and increased accumulation at the Si-SiO$_2$ interface. Similar to Figure 6a, a negligible concentration of Na$^+$ and $K^+$ ions was recorded in the sample with the shorter charging time, thus demonstrating that the methodology of ion introduction presented in this paper is a very clean process. Figure 6c demonstrates the successful incorporation of $Cs^+$ ions into SiO$_2$, which is the largest of the three ions studied. The profile shows that $Cs^+$ ions have not only been introduced into the oxide surface but have also been able to migrate through the film towards the Si-SiO$_2$ interface.
Figure 6. SIMS depth profiling of SiO$_2$ for (a) K$^+$ ions (b) Rb$^+$ ions annealed under two different field strengths and (c) Cs$^+$ ions

6. Stability of Embedded Alkali Ions

Electronic devices often function at elevated temperatures and under operational voltages.$^{31,42,74}$ Ion-charged dielectrics are therefore susceptible to heat and bias stress conditions.$^{31,42,74}$ Additionally, PV modules are exposed to UV radiation due to their placement outdoors. Accelerated ageing experiments were carried out to determine how alkali ions at the Si-SiO$_2$ interface respond to such conditions. Figure 7 tracks interface charge retention of K$^+$, Rb$^+$ and Cs$^+$ ions after embedded samples were exposed to elevated temperatures and UV radiation. Additionally, control specimens were prepared by spin coating pure DI water and IPA solvents on the oxide surface before corona charging and annealing at 300 °C. The charge stability of
all three ions over the course of 500 hours at 120 °C is shown in Figure 7a. C-V measurements were performed on MOS structures to evaluate $Q_{eff}$. An average of 5 randomly selected locations demonstrated a charge retention $>98\%$ after 120 hours for all three ions. The charge retention remained $>98\%$ after 500 hours for K$^+$ and Rb$^+$ ions whilst Cs$^+$ ions demonstrated 96% charge retention. Considering that operational solar cells do not typically exceed 70 °C, the stability demonstrated here shows that ions can withstand thermal stress sufficiently beyond that required. The control samples lost an average of 55 % charge after 120 hours. After 500 hours, there was an increase in the average $Q_{eff}$ of the control samples as well as an increase in the fluctuation in charge. This can be attributed to the high mobility of contaminants such as Na$^+$ that respond to internal concentration gradients at low temperatures giving rise to unpredictable charge distributions within the oxide. Given the negligible Na$^+$ $Q_{eff} \leq 10^{11}$ q cm$^{-2}$, these fluctuations do not have a significant impact on the measured $Q_{eff}$ of the ion-charged specimens.

Similar experiments were carried out on fresh samples to determine the stability of the ions under UV radiation. The results are shown in Figure 7b. $Q_{eff}$ of 5 samples was measured for each ion. After 120 hours, an average of 94 % and 87% charge retention was found for K$^+$ and Rb$^+$ ions respectively. Of the three ions, Cs$^+$ ions demonstrated the best charge retention of 100 %. After 500 hours, the charge retention of K$^+$ and Rb$^+$ samples lowered to 90 % and 84 %, respectively. Cs$^+$ showed the highest charge retention of 95 % after 500 hours. Given the requirement for creating a new MOS structure after each time interval, the difference in charge retention of each ion could be attributed to small variation of ionic charge within the SiO$_2$.

**Figure 8.** Stability of K$^+$, Rb$^+$ and Cs$^+$ ions over the course of 500 hours at (a) 120 °C and (b) under UV radiation.

Further tests were carried out to compare how K$^+$, Rb$^+$ and Cs$^+$ ions at the Si-SiO$_2$ interface respond to reverse biases at elevated temperatures. The ions were transported to the interface following the procedure outlined in Figure 1. A control specimen was annealed at 450 °C without any ion treatment. Following this, MOS structures were created and the samples heated to 200 °C. A reverse bias of -1 V, -5 V and -10 V was applied for a total of 60 minutes. As shown in **Figure 8**, C-V measurements were taken every 10 minutes to record changes in $Q_{eff}$. Figure 8a compares the charge retention of all three ions held at a reverse bias of -1 V, equivalent to a field of $-10^5$ V cm$^{-1}$. Rb$^+$ and Cs$^+$ ions show negligible change over the course of 60 minutes. On the other hand, K$^+$ ions show a 13 % loss in $Q_{eff}$ after the first 10 minutes.
and 42 % loss after 60 minutes. In Figure 8b, a stronger reverse bias of -5 V, equivalent to a field of \(-5 \times 10^5\) V cm\(^{-1}\), was applied. Approximately 75 % of K\(^+\) charge is lost after the first 10 minutes, followed by \(-90\ %\) depletion after 60 minutes. The Rb\(^+\) ion concentration falls by 12 % in the first 10 minutes and by 29 % after 60 minutes. Cs\(^+\) ions demonstrate excellent stability, losing just \(-5\ %\) of its initial \(Q_{\text{eff}}\) after a total of 60 minutes. The results after applying a bias of -10 V, equivalent to a field of \(-10^6\) V cm\(^{-1}\), are shown in Figure 8c. The decline of K\(^+\) charge at the interface follows a similar trend to the results in Figure 10b. The final value of \(7.8 \times 10^{11}\) q cm\(^{-2}\) is comparable to the control’s interface charge of \(3.2 \times 10^{11}\) q cm\(^{-2}\). The Rb\(^+\) sample lost 41 % of its \(Q_{\text{eff}}\) within the first 10 minutes and a further 20 % by the end of 60 minutes. The Cs\(^+\) sample showed the most gradual degradation, losing 12 % of its initial \(Q_{\text{eff}}\) after 60 minutes.

The endurance of ionic charge is critical in the operation of electret-based devices. These results demonstrate that the larger the ionic radius of the alkali ion, the better the stability and charge retention at the Si-SiO\(_2\) interface. The reported endurance of K\(^+\) ion electrets under vacuum at room temperature is 400 years, however, at a temperature of 65 °C the lifespan drops to 8 years.\(^{23}\) It is probable that under harsh atmospheric conditions, this lifespan would be even lower. The use of Rb\(^+\) and Cs\(^+\) ions in SiO\(_2\) would be expected to demonstrate superior longevity.

**Figure 8.** Stability of K\(^+\), Rb\(^+\) and Cs\(^+\) ions at the Si-SiO\(_2\) interface under a reverse bias of (a) -1 V (b) -5 V and (c) -10 V at 200 °C over 60 minutes. Dashed lines are a guide to the eye.

### 7. Conclusion

In this paper, the successful incorporation of K\(^+\), Rb\(^+\) and Cs\(^+\) ions into SiO\(_2\) has been demonstrated. This is the first time that alkali ions larger than K\(^+\) have been shown to be mobile across a SiO\(_2\) thin film. Versatile techniques of incorporating alkali ions into SiO\(_2\) have been presented here as well as methods of charge tuning. For each ion a comprehensive model of ion migration through SiO\(_2\) has been developed. This model demonstrates the dependency of ion kinetics on temperature and surface fields. It was determined that surface electric fields affect ionic conduction through SiO\(_2\), however, they do not influence the activation energy of injection. Additionally, the stability of each ion at the Si-SiO\(_2\) interface was evaluated. It was found that all three ions showed excellent stability at 120 °C with >96 % charge retention after 500 hours. Between 84 -- 95 % charge retention was measured after 500 hours under UV radiation. Under reverse bias, the larger alkali ions demonstrated significantly better stability than K\(^+\) ions. Rb\(^+\) ions were observed to withstand an electric field of \(-10^5\) V cm\(^{-1}\) whilst Cs\(^+\) ions presented excellent stability up to a field strength of \(-5 \times 10^5\) V cm\(^{-1}\) at 200 °C. Overall,
these results demonstrate the advantages of ion-charged dielectrics as a promising thin film electret material. The versatility of this system allows exploitation in numerous applications, and opens possibilities for new device architectures where field effect can be used effectively.

**Supporting Information**

Details of the code execution and corona charge decay measurements are included in the supporting information, which is available from the Wiley Online Library or from the author. All experimental data published in this article can be downloaded from [http://ora.ox.ac.uk](http://ora.ox.ac.uk).

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