

Application of Mass Transport in Solid Electrolyte Films in Tunable Microelectromechanical Resonators

M. N. Kozicki^{*}, C.L. Brown III^{*}, M. Mitkova^{*}, S. Enderling^{**}, J. Hedley^{***}, and A.J. Walton^{**}

^{*}Center for Solid State Electronics Research, Arizona State University, Tempe, AZ 85287, USA

^{**}Scottish Microelectronics Centre, University of Edinburgh, Edinburgh, EH9 3JF, UK

^{***}Department of Mechanical Engineering, University of Newcastle upon Tyne, NE1 7RU, UK

ABSTRACT

This paper reports on Ag-Ge-Se solid electrolyte films which can support the rapid net displacement of metal mass from a silver source to a target location within a MEMS device at low voltage and current. This displacement of mass can be used to alter material parameters and we have demonstrated a tunable MEMS resonator using this principle. In this application, the electrodeposited mass is made to form on a suspended polycrystalline silicon beam to change both its vibrating mass and stiffness, without significantly degrading the Q-factor. The paper includes some of the initial results from the resonator work and places particular emphasis on the solid state electro-deposition process and its relationship to the electrolyte composition.

Keywords: microelectromechanical resonator, tuning, solid electrolyte, chalcogenide, electrodeposition.

1 INTRODUCTION

An interesting materials science and engineering challenge, relating to microelectromechanical systems (MEMS), has arisen in recent times. There are many potential uses for microelectromechanical resonators in radio frequency (RF) systems due to their extremely high Q-factors but it is extremely difficult to fabricate a component which has an accurately defined resonant frequency. Nanoscale statistical irregularities caused by the nature of the materials, deposition processes, and lithography and etch methods, lead to significant distribution in mass and stiffness and both these parameters are critical in defining the resonant frequency. Even environmental factors such as oxidation or the condensation of airborne vapors can alter the vibrating mass after the structure has been fabricated. A method of *in situ* frequency tuning is therefore necessary, preferably using an electrical control signal, if microelectromechanical resonators are to reach their full potential in integrated RF communications systems.

We report on the initial results of a study involving a novel materials scheme that uses a solid electrolyte-electrodeposit system based on germanium selenide glass doped with silver, which holds great promise as a means for dynamic tuning of resonant structures. These Ag-Ge-Se

ternary materials are known to be excellent solid electrolytes due to the high mobility and availability of silver ions [1] and as such can be used to move significant amounts of ionic silver over distances of many microns via a combination of ion transport and electrodeposition/reduction [2]. This displacement of metal can be used to alter the vibrating mass and stiffness of a resonator element, thereby altering its resonant frequency. To enable the characterization of this new tuning approach, a suspended polycrystalline silicon beam test structure has been fabricated and the initial results from the electrical tuning of this are most promising [3].

This paper focuses on the material system which makes this tuning system possible, with particular emphasis being placed on the solid state electrodeposition process and its relationship to the Ag-Ge-Se electrolyte composition. Some of the key results from the suspended beam test structure are also reported.

2 MATERIAL SYSTEM

Many inorganic and organic materials can conduct ions to some extent but it is the Ag-Ge-Se ternaries that are of particular interest to us in MEMS device applications as they exhibit high ion mobility at normal device operating temperatures, are easy to form as thin films on devices, and exhibit good thermal stability during subsequent processing. An example of a ternary electrolyte that we have studied extensively is $\text{Ag}_{0.33}\text{Ge}_{0.20}\text{Se}_{0.47}$, [4] which is essentially a glassy Ge-rich backbone mixed with a Ag_2Se phase in the form of dispersed nanoscale *superionic* regions. The distinctive nanostructure of this material leads to a stable solid electrolyte that has high ion mobility (as much as $10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$) even though its resistivity is relatively large ($100 \Omega\cdot\text{cm}$ or greater) [5].

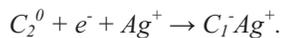
2.1 Ag-Ge-Se electrolytes

Our ternary electrolytes are formed in a two step process in which a binary (Ge-Se) base glass is deposited first and then capped with a thin silver film, the two layers being combined by *photodissolution*. The Ge content of the binary typically ranges from 20 to 40 at.%, the exact choice being dependent on the electrodeposit morphology required (discussed later). The base glass deposition is performed at or near room temperature so that previously-formed

structures will not suffer thermal damage. We use a semi-Knudsen evaporation cell to maintain the vapor flux/deposited film stoichiometry. Silver deposition is also performed using evaporation without breaking vacuum so as to prevent the formation of an oxide diffusion barrier on the surface of the glass.

For the photodissolution process, we typically use a ultraviolet source wavelength of 405 nm and power density around 5 mW/cm² for 10 minutes. The silver film thickness is kept to less than 25 nm to allow sufficient light to penetrate to the interface to stimulate the photodissolution process in a reasonable amount of time. "Saturation" of the base glass occurs when the diffusing silver reacts with all available chalcogen atoms and so the amount of Ag at saturation actually depends on the amount of chalcogen in the base glass, reaching 47 at.% for a base glass that starts with 80 at. % chalcogen [6]. A 20 nm thick silver film will completely saturate a 50 nm thick film of base glass when the photodissolution is driven to completion, leaving an extremely thin and typically discontinuous metallic silver film on the surface which can be removed using Fe(NO₃)₃ solution. To avoid the excess Ag etching step, a thicker base glass film (e.g., 80 nm) could be used with a 15 - 20 nm silver film so that all the silver is driven into the surface but the entire film thickness would not be silver saturated in this case. "Sub-saturated" electrolytes will still support electrodeposition but growth rates are typically reduced as there is obviously less Ag available.

The dissolution process results in the formation of bonds with the host matrix according to the reaction:



This reaction describes the transition of an initially twofold covalently bonded chalcogenide atom (C_2^0) into a C_1^- charged unit. This latter species possesses only a single covalent bond and an excess electron that establishes an ionic bond with the Ag^+ . The possible number of these bond-units is high as chalcogenide glasses are uniquely capable of forming a large number of single C_1^- centers under the light illumination. This not only allows photodissolution to proceed so readily but also results in the necessary structure for the solid electrolyte in which plentiful silver ions are weakly held on the large numbers of negatively charged chalcogen sites. The ions easily move from site to site under the influence of an electric field and so the ion mobility is relatively high.

2.2 Electrodeposit morphology

As can be seen from the discussion on the nature of the electrolyte above, only the positively charged ions are able to move and the negative charge centers are fixed in the electrolyte. This means that a charge imbalance (and associated electric field) will arise if reduced ions are not replaced by the oxidation of metal at the anode – the anode must therefore contain Ag if electrodeposition is to proceed.

Electrodeposition, which results in a net decrease in ion concentration at the cathode, creates a driving force to achieve simultaneous oxidation at the anode. The deposition process will only continue as long as there is oxidizable material present and so the mass of silver at the anode must be at least as great as the mass to be electrodeposited. Electrodeposition also requires an applied bias above a particular threshold to overcome the effects of the cathodic barrier. The intrinsic potential difference necessary to do this is typically only a few hundred mV and this must be dropped across the polarized double layer at the cathode. The specific resistance of the polarized region is in the order of $10^{10} \Omega \cdot \mu\text{m}^2$ [7]. Note that long structures that have a high series resistance will require higher voltages to initiate electrodeposition as most of the applied voltage will be dropped across the electrolyte.

The ions nearest the electron-supplying cathode will be reduced first. Statistical non-uniformities in the ion concentration and in the topography of the electrode will tend to promote localized deposition or nucleation rather than blanket plating on the cathode. However, even if multiple nuclei are formed, the one with the highest field and best ion supply will be favored for subsequent growth, extending out from the cathode as a single metallic feature. The electrodeposition of metal on the cathode does not mean that ions entering from the oxidizable anode have to travel the entire length of the structure to replace those that are reduced. The ion closest to the reduced ion will move to the vacated negative site on the hosting material and those upstream will do likewise, each filling the vacated site of the one downstream, until the last vacated space closest to the anode is filled by the incoming ion. So the ion current is actually a ripple effect, known in electrochemistry as a *coordinated motion*. Since the electrodeposit is physically connected to the cathode, it can supply electrons for subsequent ion reduction. So the growing electrodeposit will harvest ions from the electrolyte, plating them onto its surface to extend itself outwards from the cathode. This can lead to electrodeposits that are several hundred microns in length. Since each ion deposited on the growing electrodeposit corresponds to one that has been removed from the metal source, the net effect is a shift of mass from the anode to the cathode, even though in the initial stages, the electrodeposit is actually made up of reduced ions from the electrolyte itself.

Even though ion mobility can be high in Ag-Ge-Se solid electrolytes, it frequently is not mobility that limits the rate of the growth process. The growth occurs at the cathode double layer and this is typically only a few tens of nm wide so a few hundred mV will create a field of 10^5 V/cm. This leads to an effective ion velocity of 1 m/s if the mobility is 10^{-3} cm²/V.s. We can expect the ions to arrive at the growing electrodeposit from the surrounding electrolyte at this rate, adding to it to propel its growth forward at a considerable velocity. However, Faraday's Law prevails in these systems and so the amount of material electrodeposited equals the amount of charge

supplied by the external circuit. Each nm^3 of silver deposited contains nearly 60 atoms on average and this would require around 10^{-17} C of charge. An electrodeposit that is 10 nm high, 10 μm wide, and 100 μm long would therefore require around 10^{-7} C to form. A 1 nA current would take 100 seconds to supply this charge and so, to a first order approximation, the average growth rate would be only 1 $\mu\text{m}/\text{s}$. Clearly, a higher applied voltage would drive more current and this would increase the growth rate.

The general nature of the morphology of the silver deposits on our electrolytes corresponds closely to those reported in the literature, particularly for diffusion-controlled processes such as diffusion-limited aggregation (DLA), described first by Forrest and Witten [8]. However the nucleation points from which the electrodeposits grow are related to the presence of excess Ag ions in the electrolyte surface and this means that the composition of the electrolyte will have a profound effect on electrodeposit morphology. In the case of $\text{Ge}_{0.20}\text{Se}_{0.80}$ glasses, we observe a great number of randomly distributed deposits with microscale to nanoscale dimensions covering the surface of the films, as shown in Figure 1. In the case of the Ge-rich glasses ($\text{Ge}_{0.40}\text{Se}_{0.60}$), we see the growth of “isolated” electrodeposits [2] as illustrated in Figure 2. Between these two limiting cases there are compositions that give intermediate results. Indeed, as will be seen in the next section, we chose a $\text{Ge}_{0.30}\text{Se}_{0.70}$ base glass composition in our resonator device studies to promote the formation of relatively thick but continuous elongated electrodeposits along the length of the beam.

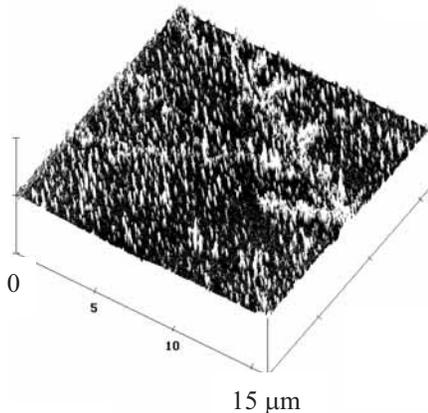


Figure 1: Atomic force microscope (AFM) analysis (3D topographical scan) of Ag electrodeposit grown on Ag-saturated $\text{Ge}_{0.20}\text{Se}_{0.80}$. The growth is continuous and the maximum electrodeposit height is a few tens of nm [2].

3 TEST STRUCTURE AND RESULTS

The suspended beam resonator test structure is shown schematically in Figure 3(a). A 1 μm thick polycrystalline

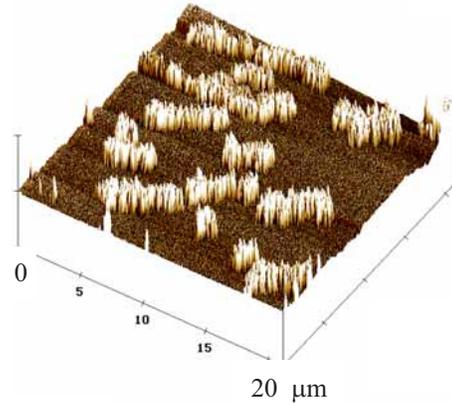


Figure 2: Atomic force microscope analysis (3D topographical scan) of Ag electrodeposit grown on Ag-saturated $\text{Ge}_{0.40}\text{Se}_{0.60}$. The growth appears discontinuous and the maximum electrodeposit height is in the order of 100 nm [2].

silicon layer was deposited on 2 μm of PECVD silicon dioxide, patterned, and then released to form the resonator. Multiple beam lengths were created, from 75 to 200 μm , all 15 μm wide. Note that for this particular fabrication scheme, no wet processing was used in subsequent steps to avoid damage to the released beams.

Following the release step, 80 nm of $\text{Ge}_{0.30}\text{Se}_{0.70}$ base glass was deposited over the entire sample, followed by 15 nm of Ag, and the metal was then photodiffused to form the electrolyte (processing details were the same as those described in the previous section). Note that the relative layer thicknesses allowed complete Ag dissolution, leaving no excess metal on the surface of the electrolyte, but led to a slightly sub-saturated electrolyte. In addition, the undercut created by the oxide etch ensured that the electrolyte on the surface of the beam was completely disconnected from the electrolyte on the substrate surface, even though we used blanket (unpatterned) electrolyte layer deposition. The anode silver pad, 50 nm thick, was evaporated through a metal shadow mask and 500 nm of aluminum was then deposited through another shadow mask to form bonding pads at both ends of the beam.

The modified resonator was fixed into an appropriate package and wire bonded to facilitate electrical testing. The package was placed on a piezoelectric chuck in a vacuum chamber and the beam movement measured using a laser deflectometer. Figure 3(b) shows a micrograph of a test device with an elongated dendritic electrodeposit, grown at 3V for 16 minutes, that extends along the length of a 150 μm beam from the cathode to the anode. Note that the relatively slow growth was due to the sub-saturation of the electrolyte, as discussed in the previous section. Figure 4 shows the effect of the magnitude of the applied voltage on a longer (200 μm) beam. Each time the voltage was increased it was held at this value for 10 minutes before the

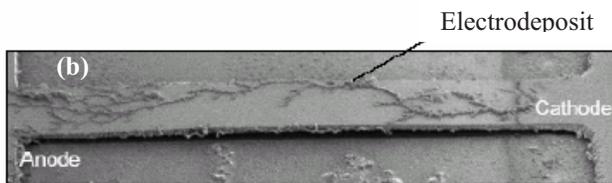
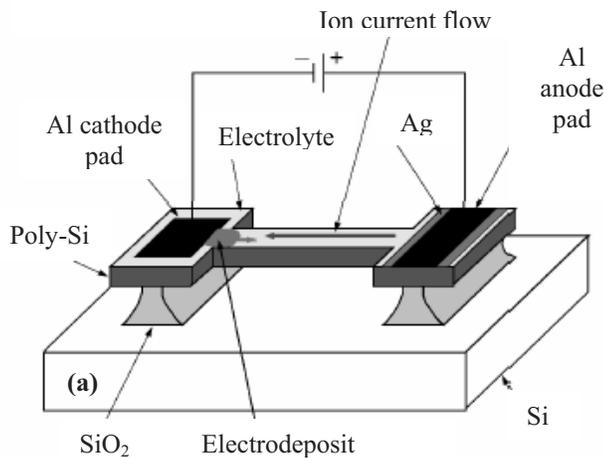


Figure 3: (a) Schematic of resonator device showing anode and cathode structures on the fixed regions. (b) Micrograph of electrodeposit grown at 3V for 16 minutes.

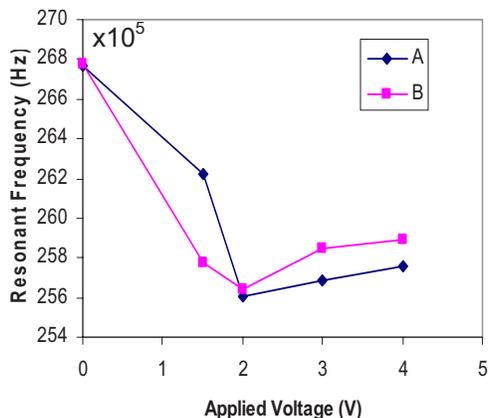


Figure 4: Effect of applied voltage on the resonant frequency of a 200 μm long beam. Line A - measurement after 10 minutes at each growth voltage; line B - after a 5 minute settling time with no bias.

resonant frequency was measured (line A). After 5 minutes of settling time, the resonant frequency was measured again (line B) to ensure that the frequency change was not due to heating effects caused by the growth and measurement conditions. The graph clearly shows a decrease in resonant frequency from the starting value of 268 kHz to a minimum at 2V around 256 kHz, a reduction of 4.5%. A slight rise in frequency occurs for higher bias, possibly due to the

stiffening of the beam due to the thickening of the electrodeposit. Figure 5 shows the corresponding Q-factor of the resonator in Figure 4 as a function of applied voltage. The Q-factor peaks at a value over 3000 at 2 V, most probably due to the mass/stiffness of the electrodeposited metal near the anchor regions.

4 CONCLUSIONS

We have successfully demonstrated the use of solid electrolyte films in the tuning of microelectromechanical beam resonators. Using a $\text{Ge}_{0.30}\text{Se}_{0.70}$ base glass photodiffused with Ag leads to continuous elongated electrodeposits at low applied voltage that alter the mass and perhaps the stiffness of the vibrating element. This leads to a substantial change in resonant frequency without reduction in Q-factor.

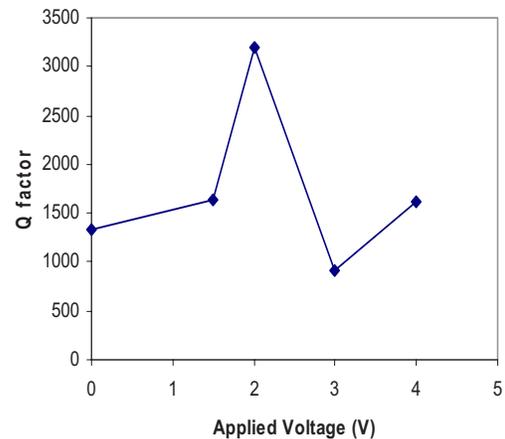


Figure 5: Q-factor as a function of the applied voltage from the tuning experiment of Figure 4.

REFERENCES

- [1] M. Kawasaki, J. Kawamura, Y. Nakamura, M. Aniya, *Sol. State Ion.*, **123**, 259 (1999).
- [2] M.N. Kozicki, M. Mitkova, J.P. Aberouette, *Physica E* **19**, 161 (2003).
- [3] S. Enderling, C. L. Brown III, M. Balakrishnan, J. Hedley, J.T.M. Stevenson, S. Bond, C.C. Dunare, A.J. Harris, J.S. Burdess, M. Mitkova, M.N. Kozicki, and A.J. Walton, *IEEE MEMS 05*, Miami, Florida, 2005.
- [4] M.N. Kozicki, M. Mitkova, J. Zhu, and M. Park, *Microelectronic Engineering*, vol. 63, 155 (2002).
- [5] T. Kawaguchi, S. Maruno, and S.R. Elliott, *J. Appl. Phys.*, vol. 79, 9096 (1996).
- [6] M. Mitkova, M.N. Kozicki, H.C. Kim, T.L. Alford, *J. Non-Cryst. Sol.* Vol. 338–340, 552 (2004).
- [7] W.C. West, K.Sieradzki, B. Kardynal, and M.N. Kozicki, *J. Electrochem. Soc.*, **145**, 2971 (1998).
- [8] S.R. Forrest and T.A. Witten Jr., *J. Phys. A* **12**, L109 (1972).