Photoelectrochemical epitaxy of silver oxide clathrate \(\text{Ag}_7\text{O}_8\text{M} (\text{M} = \text{NO}_3, \text{HSO}_4)\) on rutile-type Nb-doped TiO\(_2\) single crystals

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Silver oxide clathrate \(\text{Ag}_7\text{O}_8\text{M} (\text{M} = \text{NO}_3, \text{HSO}_4)\) compounds were synthesized photoelectrochemically on rutile-type Nb-doped TiO\(_2\) single-crystal substrates. Epitaxial crystal growth was achieved for some clathrate compositions and substrate surface orientations, where commensurate growth is possible due to lattice matching between the pseudo lattice of the clathrate \(\text{Ag}_6\text{O}_8\) cages and the TiO\(_2\) surface, similar to the well-known case of epitaxial \(\text{CdO}\) growth on single-crystal substrates. Particularly for the growth of \(\text{Ag}_7\text{O}_8\text{NO}_3\) on Nb-doped TiO\(_2\)(110), fully (111)-oriented epitaxial crystallites without any other orientations were obtained. The selectivity for \(\text{Ag}_7\text{O}_8\text{NO}_3\) growth and the suppression of the formation of by-products, such as \(\text{O}_2\), were found to depend on the electrode potential. The highest selectivity was obtained at +0.2 V vs. Ag in a 0.01 M AgNO\(_3\) solution. An investigation of \(\text{Ag}_7\text{O}_8\text{M}(\text{MM}) \) (\(\text{M} = \text{NO}_3, \text{M} = \text{HSO}_4\)) depositions from solutions with different AgNO\(_3\) and Ag\(_2\)SO\(_4\) mixing ratios showed that the growth of \(\text{Ag}_7\text{O}_8\text{HSO}_4\) is much faster than that of \(\text{Ag}_7\text{O}_8\text{NO}_3\). The process of incorporating monovalent \(\text{M} \) anions into the clathrate \(\text{Ag}_6\text{O}_8\) cages was identified as the rate-limiting step for the growth of silver oxide clathrate compounds.

1. Introduction

Silver oxide clathrates with a general formula of \(\text{Ag}_7\text{O}_8\text{M}\) are a class of clathrate compounds where \(\text{M}\) is a monovalent molecular anion that is surrounded by \(\text{Ag}_6\text{O}_8\) cages.\(^1\) The possible molecular anions in silver oxide clathrates include \(\text{NO}_3\), \(\text{HSO}_4\), \(\text{ClO}_4\), \(\text{F}_2\text{H}_2\), \(\text{BF}_4\), \(\text{PF}_6\), and \(\text{HCO}_3\),\(^2\) with some of the compounds exhibiting superconductivity at low temperatures, such as \(\text{Ag}_7\text{O}_8\text{NO}_3\) that has a \(T_c\) of 1.04 K.\(^5,6\) As is evident from the chemical formula, a \(\text{Ag}_6\text{O}_8\) cage contains \(\text{Ag}\) ions in multiple valence states, including \(\text{Ag}^+, \text{Ag}^{2+}\), and \(\text{Ag}^{3+}\). Silver oxide clathrate compounds can therefore be synthesized only under strongly oxidizing conditions; as a result, they are thermodynamically unstable and are likely to undergo self-decomposition into \(\text{AgO}_2\) and other derivatives in air even at room temperature.\(^7\)

So far, several different methods of synthesizing \(\text{Ag}_7\text{O}_8\text{M}\) have been reported, but depending on the concentration of \(\text{Ag}^+, \text{the pH, and the choice of counter anion}, \text{most methods lead to the formation of various simple binary silver oxides, such as}\ \text{Ag}_7\text{O}_4, \text{Ag}_7\text{O}_4, \text{Ag}_3\text{O}_4, \text{Ag}_2\text{O}_3, \text{and Ag}_2\text{O}_2, \text{in addition to the desired clathrate phase.}^{7,11}\) Electrochemical oxidation in a 5 M AgNO\(_3\) aqueous solution with pH = 1.45 is usually preferred for the synthesis of \(\text{Ag}_7\text{O}_8\text{NO}_3\), using a Pt electrode that is biased beyond the \(\text{Ag}_2\text{O}_3\text{NO}_3\) equilibrium potential of +1.59 V vs. the standard hydrogen electrode potential (SHE).\(^6\) We have shown earlier that \(\text{Ag}_7\text{O}_8\text{NO}_3\) films can be synthesized photocatalytically under ultraviolet (UV) light irradiation in an aqueous AgNO\(_3\) solution either directly on Nb- or La-doped SrTiO\(_3\)(001) single crystals.\(^12\) \(\text{Ag}_7\text{O}_8\text{NO}_3\) is metallic among many photo-oxidized products, and thus the photo-deposition process of \(\text{Ag}_7\text{O}_8\text{NO}_3\) on substrates that have been coated with an epitaxial ferroelectric PbTiO\(_3\) thin film can be used for an efficient domain switching to pole a large area because the metallic \(\text{Ag}_7\text{O}_8\text{NO}_3\) can stabilize the resultant polar surface.\(^13-15\) A common feature of all these surfaces is the presence of valence band levels that are derived predominantly from O 2p states and are thus more positive than the equilibrium potential. Similar light-induced deposition of \(\text{Ag}_7\text{O}_8\text{NO}_3\), though not photocatalytically, has been observed on GaAs substrates when synchrotron X-rays were used as a light source.\(^16\) More recently, we also demonstrated photoelectrochemical synthesis of \(\text{Ag}_7\text{O}_8\text{NO}_3\) on Nb-doped SrTiO\(_3\)(001) single-crystal electrodes in a AgNO\(_3\) solution and
discussed the role of the electrode potential in this photochemical process.\(^\text{17}\)

Despite the availability of different synthesis methods, the crystal growth mechanism of silver oxide clathrate compounds is still very poorly understood. In particular, it is not clear if silver oxide clathrates can be epitaxially grown on appropriate lattice-matched single-crystal substrates. There is a growing interest in developing electrochemical room-temperature epitaxy techniques, often termed “electrochemical epitaxy”.\(^\text{18}\) However, the growth of silver oxide clathrate compounds is usually not epitaxial, even when single-crystal electrodes, like Pt(100), Pt(111), Pt(110)\(^\text{10}\) and Nb-doped SrTiO\(_3\)(001) are used, probably due to the large difference in the crystal structures of the clathrate films and the single-crystal substrate electrodes. So far, only out-of-plane orientation control has been achieved in the growth of Ag\(_7\)O\(_8\)NO\(_3\) on Pb–Ti–O buffer layers\(^\text{11}\) but there is no conclusive data on epitaxial growth of any silver oxide clathrate compounds. If epitaxy for these materials can be achieved, a new guiding principle may be developed for epitaxial growth of materials that have very different crystal structures from the substrate.

In the present work, we therefore examine the possibility of epitaxial photoelectrochemical growth of Ag\(_7\)O\(_8\)NO\(_3\) and Ag\(_7\)O\(_8\)HSO\(_4\) on Nb-doped TiO\(_2\) single crystals under UV irradiation at a well-controlled electrode potential and compare the results with earlier studies that used Nb-doped SrTiO\(_3\)(001) as a substrate. Since the clathrate formation reaction competes with water photo-oxidation, we take a careful look at the electrode potential dependence of the reaction selectivity against the formation of by-products, such as O\(_2\). The crystal growth mechanism of silver oxide clathrates is studied by investigating the growth behaviour of Ag\(_7\)O\(_8\)(MM\(^\prime\)) \((\text{MM} = \text{NO}_3, \text{M}^\prime = \text{HSO}_4)\) in mixtures of AgNO\(_3\) and Ag\(_2\)SO\(_4\) solutions at different mixing ratios. We identify the rate-limiting step for the growth of silver oxide Ag\(_7\)O\(_8\)M clathrate compounds and show that single-phase Ag\(_7\)O\(_8\)NO\(_3\) can be epitaxially grown on Nb-doped TiO\(_2\)(110) surfaces.

2. Experimental section

We used single-crystal n-type 0.5 wt% Nb-doped rutile TiO\(_2\) substrates with (110), (101), (100), and (001) surface cuts from Shinkosha.\(^\text{19}\) Ohmic substrate contacts were made by coating the backside of the crystals with an In–Ga alloy and attaching copper wires with silver paste. All parts of the samples, except for the middle part of the front surface, were covered with epoxy resin to avoid leak currents in the electrochemical cell. The photoelectrochemical synthesis was performed at room temperature in a three-electrode electrochemical cell, using a Pt plate counter electrode and a silver wire reference electrode. The electrolytes used in this study included 0.01 M AgNO\(_3\) and 0.01 M Ag\(_2\)SO\(_4\) aqueous solutions, and mixtures of AgNO\(_3\) and Ag\(_2\)SO\(_4\) solutions with different mixing ratios. The photoelectrochemical reaction was carried out under UV light illumination from a high-pressure Hg lamp (Ushio, USH-150SC) at a constant flux of 28 mW cm\(^{-2}\) and the photocurrent was recorded at a sampling rate of 5 Hz. The light intensity was measured with an integrating light counter at 254 nm (Ushio, U1T-150-A). The electrode potential was set in the range between −0.5 and +1 V vs. Ag. After photoelectrochemical treatment, the deposited materials were first identified by \(\theta\)-\(2\theta\) X-ray diffraction (XRD) analysis (MAC Science SRA M18XHF22), followed by, if needed, X-ray \(\Phi\) scan analysis (PANalytical X'Pert PRO MRD) in order to investigate the epitaxial in-plane orientation of the Ag\(_7\)O\(_8\)NO\(_3\) and Ag\(_7\)O\(_8\)HSO\(_4\) crystals with respect to the TiO\(_2\) substrate lattice. The morphology of the Ag\(_7\)O\(_8\)NO\(_3\) and Ag\(_7\)O\(_8\)HSO\(_4\) crystals was observed by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) was used to estimate the total volume and the composition of the deposition products (Hitachi S-4000). The photocatalytic reaction kinetics on Nb-doped TiO\(_2\) was investigated by measuring the relative selectivity \(\sigma\) between Ag\(_7\)O\(_8\)NO\(_3\) and other by-products, such as O\(_2\). The selectivity is defined as

\[
\sigma = \frac{I(\text{Ag/Ti})}{Q_{\text{photo}}}
\]

where \(I(\text{Ag/Ti})\) is the measured EPMA intensity ratio of Ag and Ti, and \(Q_{\text{photo}}\) is the total electrical charge conveyed per unit surface area by the photocurrent during the photoelectrochemical reaction.

![Fig. 1. A set of \(\theta\)-\(2\theta\) XRD patterns of photoelectrochemically deposited Ag\(_7\)O\(_8\)NO\(_3\) grown on Nb-doped TiO\(_2\) (a) (110), (b) (101), (c) (100), and (d) (001) single-crystal substrates in a 0.01 M AgNO\(_3\) solution at an electrode potential of +0.3 V vs. Ag. The deposition time was 2 h. All plots are shown on a logarithmic scale.](image-url)
3. Results and discussion

3.1. Growth of Ag$_7$O$_8$NO$_3$ on Nb-doped TiO$_2$ single crystals

Fig. 1 shows $\theta$–2$\theta$ XRD patterns of Ag$_7$O$_8$NO$_3$ crystals that were photoelectrochemically deposited in 2 hours on Nb-doped TiO$_2$ (110), (101), (100), and (001) single-crystal substrates in 0.01 M AgNO$_3$ at an electrode potential of +0.3 V vs. Ag. Diffraction peaks were observed at $2\theta = 31.28^\circ$, 36.27$^\circ$, 52.26$^\circ$, and 65.56$^\circ$, revealing that only Ag$_7$O$_8$NO$_3$ was deposited on the TiO$_2$ substrates, irrespective of the crystal face. No other peaks that could be assigned to binary silver oxides were detected. All XRD patterns in Fig. 1 show reflections of (111)-oriented Ag$_7$O$_8$NO$_3$ crystals. In particular, Fig. 1(a) shows the 222 peak for the sample grown on TiO$_2$(110) has the highest intensity, even though the deposition times are identical. As the FWHM values for the $\theta$–2$\theta$ scans are not so different, the highest intensity of Ag$_7$O$_8$NO$_3$ on TiO$_2$(110) is due to its unique out-of-plane orientation.

The crystal quality of Ag$_7$O$_8$NO$_3$ was further analyzed by visualizing the grain structure by SEM, as shown in Fig. 2. It is clear that a few large faceted crystals and many small grains grew on TiO$_2$(101), (100), and (001) substrates, suggesting a polycrystalline nature of Ag$_7$O$_8$NO$_3$ on these surfaces. Only Fig. 2(a) shows large hexagonal crystal platelets with a unique in-plane orientation growing on the TiO$_2$(110) substrate. This implies epitaxial growth of (111)-oriented Ag$_7$O$_8$NO$_3$ crystals on the TiO$_2$(110) substrate. The thickness of each Ag$_7$O$_8$NO$_3$ platelet could be estimated to be in a range of a few hundred nanometers from a cross-sectional SEM image (not shown). The epitaxial relationship was determined from the $\Phi$ scans recorded for the TiO$_2$(111) and Ag$_7$O$_8$NO$_3$(400) reflections, as shown in Fig. 3. There are six Ag$_7$O$_8$NO$_3$(400) peaks and two TiO$_2$(111) reflection peaks, which means that (111)-oriented Ag$_7$O$_8$NO$_3$ grew epitaxially on TiO$_2$(110) in two equivalent domains that are rotated by 180$^\circ$ with respect to each other. The in-plane relationship between the Ag$_7$O$_8$NO$_3$ crystals and the TiO$_2$(110) substrate is summarized in Table 1, revealed that some Ag$_7$O$_8$NO$_3$ crystals grew epitaxially on other TiO$_2$ crystal planes as well. For example, the data in Fig. 1 shows that (111)-oriented Ag$_7$O$_8$NO$_3$ crystals were always present, regardless of the TiO$_2$ substrate orientation. These photoelectrochemical deposition results are consistent with our earlier work on electrochemical deposition of clathrates on Nb:SrTiO$_3$(001) substrates, and photodeposition on Nb- or La-doped SrTiO$_3$(001) and on PbTiO$_3$/Nb:SrTiO$_3$(001). Ag$_7$O$_8$NO$_3$ appears to have a crystal habit of preferentially growing along the (111) direction, but the selectivity for pure (111)-oriented growth is the highest for photoelectrochemical deposition on TiO$_2$(110) substrates.

![Fig. 2](image_url) SEM images of the same set of Ag$_7$O$_8$NO$_3$ samples for (a) (110), (b) (101), (c) (100), and (d) (001) single-crystal TiO2 substrates that were used for the XRD analysis in Fig. 1.

![Fig. 3](image_url) X-ray $\Phi$ scans of (a) TiO$_2$(111) and (b) Ag$_7$O$_8$NO$_3$(400) reflections for a (111)-oriented Ag$_7$O$_8$NO$_3$ sample epitaxially grown on a TiO$_2$(110) substrate. Six clathrate peaks were observed from two equivalent domains rotated by 180$^\circ$ relative to each other.

| Substrate     | Epitaxial orientation | Non-epitaxial orientation | In-plane direction | In-plane direction |
|---------------|-----------------------|----------------------------|--------------------|--------------------|
| TiO$_2$(110)  | [111]                 | ×                          | [112]              | [110]              |
| TiO$_2$(101)  | (111)                 |                            | [110]              | [001]              |
| TiO$_2$(100)  | (111)                 |                            | [001]              | [010]              |
| TiO$_2$(001)  | (111)                 |                            | [110]              | [010]              |

Ag$_7$O$_8$NO$_3$(111)[110]/TiO$_2$(110)[001], Ag$_7$O$_8$NO$_3$(111)[112]/TiO$_2$(110)[110] or Ag$_7$O$_8$NO$_3$(111)[112]/TiO$_2$(110)[110].
3.2. Epitaxial growth model of Ag$_7$O$_8$NO$_3$/Nb-doped TiO$_2$ interfaces

We follow earlier work by Breyfogle et al.,$^{11}$ who found that the growth orientation of Ag$_7$O$_8$NO$_3$ crystals is tunable by selecting a suitable lattice-matched and textured Pb–Ti–O bottom layer, and consider the lattice mismatch between Ag$_7$O$_8$NO$_3$ crystals and TiO$_2$ substrates. Fig. 4(a) schematically illustrates the Ag$_7$O$_8$NO$_3$ crystal structure,$^1$ showing a network composed of large face-sharing rhombicuboctahedral Ag$_6$O$_8$ cages. Silver ions are located at the centre points of the shared cage faces and in the middle of the small cubic voids in between the cages. As is illustrated in Fig. 4(b), the dominant factor determining whether commensurate epitaxial Ag$_7$O$_8$NO$_3$ crystal growth can occur on a substrate is the Ag$_6$O$_8$ cage size, which determines the lattice mismatch between the TiO$_2$ surface and the clathrate cage pseudo lattice. This is analogous to the epitaxial growth of C$_{60}$, which is another well-known molecular cage compound that can be epitaxially grown on single-crystal substrates.$^{21,22}$ The in-plane distances of the cage pseudo lattice viewed along the (111) direction are 6.993 Å and 6.056 Å. We have taken a closer look at the structure of the unreconstructed TiO$_2$(110) surface to understand the reason for the epitaxial growth of (111)-oriented Ag$_7$O$_8$NO$_3$ crystals on TiO$_2$(110) substrates. This surface consists of 5-fold coordinated titanium (Ti$_{5c}$) atoms, in-plane oxygen atoms, and bridging oxygen atoms (O$_b$), as shown in Fig. 4(c). The bridging oxygen atoms are known to have a strong effect on the chemical reaction at the interface between the TiO$_2$(110) surface and an electrolyte.$^{23}$ The distance between adjacent bridging oxygen lines is 6.495 Å. Fig. 4(d) and (e) show two possible in-plane alignments of (111)-oriented Ag$_7$O$_8$NO$_3$ crystals on the TiO$_2$(110) surface. The black closed and open circles mark the positions of Ti atoms along the O$_b$ rows and at the Ti$_{5c}$ sites, respectively, as illustrated in Fig. 4(f). The model in Fig. 4(d) clearly shows a smaller lattice mismatch than that in Fig. 4(e), and corresponds to the experimentally observed in-plane orientation as shown by the φ scan in Fig. 3. In general, it is difficult to stabilize a triangular lattice, such as that of the (111)-oriented Ag$_7$O$_8$NO$_3$ crystals, on a rectangular lattice. However, the tetragonal TiO$_2$(110) surface has strong in-plane anisotropy, allowing the (111)-oriented Ag$_7$O$_8$NO$_3$ crystals to grow epitaxially with only moderate in-plane mismatch.

3.3. Reaction selectivity against O$_2$ by-products

The effect of the electrode potential on the growth of Ag$_7$O$_8$NO$_3$ crystals on TiO$_2$(110) was investigated. Fig. 5 shows the relative selectivity for the formation of Ag$_7$O$_8$NO$_3$ (filled circles) as a function of the electrode potential, together with SEM images of crystals grown at electrode potentials of (a) −0.15, (b) +0.2 and (c) +0.45 V, respectively. (d) Relative selectivity of the formation of Ag$_7$O$_8$NO$_3$ (filled circles) as a function of electrode potential. Open circles correspond to the formation of Ag metal particles.
potentials of $-0.15$, $+0.2$, and $+0.45$ V. In principle, no deposition of Ag$_7$O$_8$NO$_3$ (relative selectivity = 0) should occur at negative electrode potentials vs. Ag and, as expected, the inset SEM image for the $-0.15$ V sample shows almost no growth. It is thermodynamically more likely for Ag ions to be reduced to Ag metal at negative electrode potentials and this behaviour was experimentally observed for electrode potentials $<-0.3$ V, with Ag metal deposits growing on the TiO$_2$ electrode instead of a clathrate phase. These data points are marked with open circles in Fig. 5. On the other hand, for positive electrode potentials, a gradual increase in selectivity was found up to a potential of ca. $+0.2$ V, at which point the selectivity reached a maximum and decreased again for higher potentials. The inset SEM images of the $+0.2$ V and $+0.45$ V samples show that the selectivity changes are clearly reflected in the morphology of the crystals. Based on our earlier work on the growth selectivity of Ag$_7$O$_8$NO$_3$ on Nb-doped SrTiO$_3$(001),$^{17}$ it appears that the selectivity maximum at around $+0.2$ V is a common feature of silver oxide clathrates.

A notable difference, however, is that on SrTiO$_3$ around $+0.2$ V is a common feature of silver oxide clathrates.

3.4. Comparison of the growth behaviours of Ag$_7$O$_8$NO$_3$ and Ag$_7$O$_8$HSO$_4$ on Nb-doped TiO$_2$ single crystals

The photoelectrochemical synthesis of other types of silver oxide clathrates on Nb-doped TiO$_2$ single crystals was also studied under experimental conditions that were identical except for the composition of the electrolyte. Ag$_7$O$_8$HSO$_4$ crystals were successfully obtained in a 0.01 M Ag$_2$SO$_4$ solution, while the synthesis of Ag$_7$O$_8$ClO$_4$ in a 0.01 M AgClO$_4$ solution was possible, but the absolute amount was too small to be fully characterized. We therefore compare the growth of Ag$_7$O$_8$HSO$_4$ with Ag$_7$O$_8$NO$_3$. Fig. 6 shows a set of $\theta$-2$\theta$ XRD patterns of Ag$_7$O$_8$HSO$_4$ layers that were photoelectrochemically deposited in 2 hours on Nb-doped TiO$_2$ (110), (101), (100), and (001) single-crystal substrates in 0.01 M Ag$_2$SO$_4$ at an electrode potential of $+0.3$ V vs. Ag in 2 h. All plots are shown on a logarithmic scale.

Fig. 6 A set of $\theta$-2$\theta$ XRD patterns of photoelectrochemically deposited Ag$_7$O$_8$HSO$_4$ grown on Nb-doped TiO$_2$ (a) (110), (b) (101), (c) (100), and (d) (001) single-crystal in a 0.01 M Ag$_7$O$_8$HSO$_4$ solution at an electrode potential of $+0.3$ V vs. Ag in 2 h. All plots are shown on a logarithmic scale.

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Fig. 7 SEM images of the same set of Ag$_7$O$_8$HSO$_4$ samples for (a) (110), (b) (101), (c) (100), and (d) (001) single-crystal TiO$_2$ substrates that were used for the XRD analysis in Fig. 6.
In order to rule out this possibility, simultaneous photo-deposition of Ag$_7$O$_9$(M$'$)(M = NO$_3$, M$'$ = HSO$_4$) on TiO$_2$(110) was tested by using mixtures of AgNO$_3$ and Ag$_2$SO$_4$ solutions with different mixing ratios at an electrode potential of +0.3 V vs. Ag, where any unexpected effects that would appear even when all the experimental conditions are equal will be minimized. As shown by the series of SEM images in Fig. 8, no large crystalites were formed in a pure 0.01 M AgNO$_3$ solution after a 2-hour deposition. As the concentration of Ag$_2$SO$_4$, $c_{\text{Ag}_2\text{SO}_4}$, in the mixed solution increased, the number of large crystals also increased, reaching a maximum size for $c_{\text{Ag}_2\text{SO}_4} = 0.01$ and decreasing for higher Ag$_2$SO$_4$ concentrations. It is noted that a very small, e.g. 20%, increase of Ag$^+$ in the solution by adding Ag$_2$SO$_4$ ($c_{\text{Ag}_2\text{SO}_4}$ is 0.001 M) is enough to cause a big change in the morphology and growth rate of the silver oxide clathrate compounds. According to our previous work, the concentration dependence of the growth rate and morphology is not very strong in the photocatalytic synthesis of Ag$_7$O$_9$NO$_3$ on Nb:SrTiO$_3$(001); the observed changes may not be simply due to the Ag$^+$ concentration effect. As most of the volume of the deposited clathrate is contained in the large crystallites, the areal density of such crystals and their volume as a function of $c_{\text{Ag}_2\text{SO}_4}$ should be proportional to the total amount of photodeposited silver-oxide clathrate compounds, which can be measured from the EPMA Ag/Ti intensity ratio as shown in Fig. 9(a). On the other hand, the intensity ratio of the 400 and 222 XRD peaks, plotted as a function of $c_{\text{Ag}_2\text{SO}_4}$ in Fig. 9(b), shows a similar tendency to the Ag/Ti intensity ratio. The large crystals can thus be identified as (100)-oriented clathrate crystals. The large number of smaller plate-like crystals that can be seen in the inset of Fig. 7(a) is spread under and around the large (100) crystals and appears to have formed at the initial growth stage. These small crystallites are responsible for the weaker 222 and 444 XRD peaks in Fig. 6 and these crystallites are thus oriented along the (111) direction. As was pointed out earlier, among the silver oxide clathrates studied here, only Ag$_7$O$_9$HSO$_4$ crystals can grow along the (100) direction on TiO$_2$(110). We can therefore conclude that when mixtures of AgNO$_3$ and Ag$_2$SO$_4$ solutions are used under the present experimental conditions, the dominant (100)-oriented Ag$_7$O$_9$HSO$_4$ phase is either pure Ag$_7$O$_9$HSO$_4$ or at least a Ag$_7$O$_9$HSO$_4$-rich mixed clathrate. The preferential formation of Ag$_7$O$_9$HSO$_4$ clathrate is probably caused by the faster growth rate of Ag$_7$O$_9$HSO$_4$ crystals when compared to Ag$_7$O$_9$NO$_3$ for both (100) and (111) orientations. As can be seen in the inset of Fig. 7(a), the average size of the (111)-oriented crystals of Ag$_7$O$_9$HSO$_4$ is much smaller than that of Ag$_7$O$_9$NO$_3$ crystals in Fig. 2(a). Both images were taken after a 2-hour photodeposition run under otherwise identical conditions. This size difference can be understood in terms of the kinetic effect, i.e., a higher growth rate leads to the formation of a larger number of smaller crystals. The small (111)-oriented crystallites grown from a mixed solution may contain Ag$_7$O$_9$NO$_3$ or Ag$_7$O$_9$NO$_3$-rich mixed clathrates as well as Ag$_7$O$_9$HSO$_4$, but the volume fraction of the former must be very small due to the lower growth rate. This assumption is supported by the observation that, as shown in Fig. 9(c), the EPMA intensity ratio of S to Ag appears to be nearly constant, irrespective of the mixing ratio of the growth solution.

Fig. 8 A series of SEM images of silver oxide clathrate compounds photodeposited in solutions of AgNO$_3$ and Ag$_2$SO$_4$ with different mixing ratios at an electrode potential of +0.3 V vs. Ag in 1 h.
Furthermore, the decrease of the EPMA Ag/Ti intensity ratio, i.e., the amount of Ag₂O₃H₂SO₄ or Ag₂O₃HSO₄-rich clathrates deposited as a major product, at cₖAgSO₄ higher than 0.01 M, can be understood when considering the very narrow Ag⁺ ion concentration window of less than 0.005 M where Ag₂O₃H₂SO₄ can be synthesized by electrochemical oxidation.²

In simultaneous photodeposition of Ag₂O₃(MM') (M = NO₃, M' = HSO₄) the process that forms Ag₆O₈ cages through the oxidation of Ag⁺ ions is common for both materials and the rate-limiting step for the growth of silver oxide clathrate Ag₂O₈M compounds must therefore be a process that involves the monovalent anions. It is possible, for example, that the different incorporation kinetics of the anions inside the Ag₆O₈ cages are responsible for the observed differences in the Ag₂O₈NO₃ and Ag₂O₃HSO₄ growth rates.

4. Conclusion

We have succeeded in photoelectrochemically synthesizing silver oxide clathrate Ag₂O₈M (M = NO₃, HSO₄) compounds on Nb-doped rutile TiO₂ single-crystal substrates. An epitaxial relationship between the clathrate crystals and TiO₂ substrates was found for some combinations of the clathrate anions and substrate orientations, with a particularly clear case being the fully (111)-oriented growth of Ag₂O₈NO₃ occurring on TiO₂(110). This result has confirmed that commensurate, epitaxial lattice matching can occur between a single-crystal substrate lattice and the pseudo lattice of cages in an inorganic compound, such as the Ag₂O₈NO₃ clathrate used in this work. This work shows that such a matching is not unique to organic cage compounds like C₆₀. A certain electrode potential of ca. +0.2 V vs. Ag resulted in the preferential deposition of Ag₂O₈NO₃ over other by-products. It was found that the process of incorporating monovalent anions, such as NO₃⁻ or HSO₄⁻, into the Ag₆O₈ cages is likely the rate-limiting step in this photoelectrochemical silver oxide clathrate synthesis, leading to different growth rates of Ag₂O₈NO₃ and Ag₆O₈HSO₄.

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