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1. Introduction

Silver oxide clathrates with a general formula of Ag_7O_8M are a class of clathrate compounds where M is a monovalent molecular anion that is surrounded by Ag_6O_8 cages.¹ The possible molecular anions in silver oxide clathrates include NO₃, HSO₄, ClO₄, HF₂, BF₄, PF₆, and HCO₃,²⁻⁴ with some of the compounds exhibiting superconductivity at low temperatures, such as $Ag_7O_8NO_3$ that has a T_c of 1.04 K.^{5,6} As is evident from the chemical formula, a Ag_6O_8 cage contains Ag ions in multiple valence states, including Ag^+ , Ag^{2+} , and 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 AgO_x and other derivatives in air even at room temperature.⁷

So far, several different methods of synthesizing Ag_7O_8M have been reported, but depending on the concentration of

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Silver oxide clathrate Ag_7O_8M (M = NO₃, HSO₄) compounds were synthesized photoelectrochemically on rutile-type Nb-doped TiO₂ 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 Ag_6O_8 cages and the TiO₂ surface, similar to the well-known case of epitaxial C_{60} growth on single-crystal substrates. Particularly for the growth of $Ag_7O_8NO_3$ on Nb-doped TiO₂(110), fully (111)-oriented epitaxial crystallites without any other orientations were obtained. The selectivity for $Ag_7O_8NO_3$ growth and the suppression of the formation of by-products, such as 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 AgNO₃ solution. An investigation of $Ag_7O_8(MM')$ (M = NO₃, M' = HSO₄) depositions from solutions with different $AgNO_3$ and Ag_2SO_4 mixing ratios showed that the growth of $Ag_7O_8HSO_4$ is much faster than that of $Ag_7O_8NO_3$. The process of incorporating monovalent M anions into the clathrate Ag_6O_8 cages was identified as the rate-limiting step for the growth of silver oxide clathrate compounds.

Ag⁺, the pH, and the choice of counter anion, most methods lead to the formation of various simple binary silver oxides, such as Ag₃O₄, Ag₂O₄, Ag₂O, and Ag₂O₂, in addition to the desired clathrate phase.⁷⁻¹¹ Electrochemical oxidation in a 5 M AgNO₃ aqueous solution with pH = 1.45 is usually preferred for the synthesis of Ag₇O₈NO₃, using a Pt electrode that is biased beyond the Ag₇O₈NO₃ equilibrium potential of +1.59 V vs. the standard hydrogen electrode potential (SHE).9 We have shown earlier that Ag₇O₈NO₃ films can be synthesized photocatalytically under ultraviolet (UV) light irradiation in an aqueous AgNO₃ solution either directly on Nb- or La-doped SrTiO₃(001) single crystals.¹² Ag₇O₈NO₃ is metallic among many photo-oxidized products, and thus the photodeposition process of Ag₇O₈NO₃ on substrates that have been coated with an epitaxial ferroelectric PbTiO₃ thin film can be used for an efficient domain switching to pole a large area because the metallic Ag₇O₈NO₃ 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 Ag₇O₈NO₃, 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 Ag7O8NO3 on Nb-doped $SrTiO_3(001)$ single-crystal electrodes in a AgNO₃ solution and

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discussed the role of the electrode potential in this photochemical process.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 roomtemperature epitaxy techniques, often termed "electrochemical epitaxy".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)¹⁰ and Nb-doped SrTiO₃(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 Ag₇O₈NO₃ on Pb-Tl-O buffer layers¹¹ 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 Ag₇O₈NO₃ and Ag₇O₈HSO₄ on Nb-doped TiO₂ 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 O₂. The crystal growth mechanism of silver oxide clathrates is studied by investigating the growth behaviour of Ag₇O₈(MM') $(M = NO_3, M' = HSO_4)$ in mixtures of AgNO₃ and Ag₂SO₄ solutions at different mixing ratios. We identify the rate-limiting step for the growth of silver oxide Ag₇O₈M clathrate compounds and show that single-phase Ag₇O₈NO₃ 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.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 AgNO₃ and 0.01 M Ag₂SO₄ aqueous solutions, and mixtures of AgNO₃ and Ag₂SO₄ 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, UIT-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 θ -2 θ X-ray diffraction (XRD) analysis (MAC Science SRA M18XHF22), followed by, if needed, X-ray Φ scan analysis (PANalytical X'Pert PRO MRD) in order to investigate the epitaxial in-plane orientation of the Ag₇O₈NO₃ and Ag₇O₈HSO₄ crystals with respect to the TiO₂ substrate lattice. The morphology of the Ag₇O₈NO₃ and Ag₇O₈HSO₄ 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 TiO2 was investigated by measuring the relative selectivity σ between Ag₇O₈NO₃ and other by-products, such as O₂. The selectivity is defined as

$$\sigma = \frac{I(\text{Ag/Ti})}{Q_{\text{photo}}}$$
(1)

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



Fig. 1 A set of θ -2 θ XRD patterns of photoelectrochemically deposited Ag₇O₈NO₃ grown on Nb-doped TiO₂ (a) (110), (b) (101), (c) (100), and (d) (001) single-crystal substrates in a 0.01 M AgNO₃ 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.

3. Results and discussion

3.1. Growth of Ag₇O₈NO₃ on Nb-doped TiO₂ single crystals

Fig. 1 shows θ -2 θ XRD patterns of Ag₇O₈NO₃ crystals that were photoelectrochemically deposited in 2 hours on Nbdoped TiO₂ (110), (101), (100), and (001) single-crystal substrates in 0.01 M AgNO₃ at an electrode potential of +0.3 V vs. Ag. Diffraction peaks were observed at 2θ = 31.28°, 36.27°, 52.26°, and 65.56°,²⁰ revealing that only Ag₇O₈NO₃ was deposited on the TiO₂ 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 Ag₇O₈NO₃ crystals. In particular, Fig. 1(a) shows that the 222 peak for the sample grown on TiO₂(110) has the highest intensity, even though the deposition times are identical. As the FWHM values for the θ -2 θ scans are not so different, the highest intensity of Ag₇O₈NO₃ on TiO₂(110) is due to its unique out-of-plane orientation.

The crystal quality of Ag₇O₈NO₃ 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 TiO₂(101), (100), and (001) substrates, suggestive of a polycrystalline nature of Ag₇O₈NO₃ 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 $Ag_7O_8NO_3$ crystals on the TiO₂(110) substrate. The thickness of each Ag₇O₈NO₃ 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 Φ scans recorded for the TiO₂(111) and $Ag_7O_8NO_3(400)$ reflections, as shown in Fig. 3. There are six Ag₇O₈NO₃(400) peaks and two TiO₂(111) reflection peaks, which means that (111)-oriented Ag₇O₈NO₃ grew epitaxially on $TiO_2(110)$ in two equivalent domains that are rotated by 180° with respect to each other. The in-plane relationship between the Ag₇O₈NO₃ crystals and the TiO₂(110) substrate is



Fig. 2 SEM images of the same set of $Ag_7O_8NO_3$ 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 X-ray Φ scans of (a) TiO₂(111) and (b) Ag₇O₈NO₃(400) reflections for a (111)-oriented Ag₇O₈NO₃ sample epitaxially grown on a TiO₂(110) substrate. Six clathrate peaks were observed from two equivalent domains rotated by 180° relative to each other.

 $\begin{array}{l} \mbox{Ag_7O_8NO_3(111)[1\bar{1}0]//TiO_2(110)[001], \mbox{Ag_7O_8NO_3(111)[112]//TiO_2(110)[1\bar{1}0]} \\ \mbox{or } \mbox{Ag_7O_8NO_3(111)[11\bar{2}]//TiO_2(110)[1\bar{1}0]. \end{array}$

The FWHM value of the (111)-oriented epitaxial Ag₇O₈NO₃ film on TiO₂(110), estimated from the Φ scan, is as large as 1.815°, suggesting that the crystallinity and mosaic spread, though these two parameters cannot be independently discussed here, are significant the in-plane direction. Nevertheless, the X-ray analysis results are consistent with the SEM observation of a unique in-plane orientation of the large crystallites in Fig. 2(a). The analysis of the Φ scan data, summarized in Table 1, revealed that some Ag₇O₈NO₃ crystals grew epitaxially on other TiO2 crystal planes as well. For example, the data in Fig. 1 shows that (111)-oriented Ag₇O₈NO₃ crystals were always present, regardless of the TiO₂ substrate orientation. These photoelectrochemical deposition results are consistent with our earlier work on electrochemical deposition of clathrates on Nb:SrTiO₃(001) substrates,¹² and photodeposition on Nb- or La-doped SrTiO₃(001)¹⁷ and on PbTiO₃/Nb:SrTiO₃(001).¹³⁻¹⁵ Ag₇O₈NO₃ 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.

Table 1 Epitaxial relationship between TiO_2 substrates and photoelectrochemically deposited $Ag_7O_8NO_3$ crystals

Substrate	Ag ₇ O ₈ NO ₃	Ag ₇ O ₈ NO ₃	Ag ₇ O ₈ NO ₃	TiO ₂
	Epitaxial orientation	Non-epitaxial orientation	In-plane direction	In-plane direction
$TiO_2(110)$	(111)	×	[112] [110]	[110] [001]
$TiO_2(101)$	(100)	(111)	[001] [010]	[010] [101]
$TiO_2(100)$	(110)	(111) (100)	[001] [110]	[001] [010]
$TiO_2(001)$	(110)	(111) (100)	[001] [110]	[100] [010]

3.2. Epitaxial growth model of Ag₇O₈NO₃/Nb-doped TiO₂ interfaces

We follow earlier work by Breyfogle et al.,¹¹ who found that the growth orientation of Ag₇O₈NO₃ crystals is tunable by selecting a suitable lattice-matched and textured Pb-Tl-O bottom layer, and consider the lattice mismatch between Ag₇O₈NO₃ crystals and TiO₂ substrates. Fig. 4(a) schematically illustrates the Ag₇O₈NO₃ crystal structure,¹ showing a network composed of large face-sharing rhombicuboctahedral Ag₆O₈ 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 Ag₇O₈NO₃ crystal growth can occur on a substrate is the Ag₆O₈ cage size, which determines the lattice mismatch between the TiO₂ 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 singlecrystal 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



Fig. 4 (a) Schematic illustration of the Ag₇O₈NO₃ crystal structure in a cubic system. Blue, red, and gray spheres denote Ag, N, and O, respectively. (b) A view of the (111) surface of a Ag₇O₈NO₃ crystal. The red lines mark the outlines of the surface unit cell of the rhombicuboctahedral pseudo lattice. (c) Illustration of the TiO₂(110) surface structure. The surface layer consists of bridging oxygens (O_b), 5-fold coordinated titanium atoms (Ti_{5c}), and in-plane oxygens. (d, e) Two possible in-plane alignments of Ag₇O₈NO₃ crystals on a TiO₂(110) surface. The black open and closed circles mark the positions of the Ti_{5c} and bridging titanium sites, respectively, on the underlying TiO₂(110) surface. The configuration in (d) corresponds to the experimental results in Fig. 3, showing only a small lattice mismatch between the rhombicuboctahedral cage lattice and the bridging oxygens on the TiO₂(110) surface.

unreconstructed TiO₂(110) surface to understand the reason for the epitaxial growth of (111)-oriented Ag₇O₈NO₃ crystals on TiO₂(110) substrates. This surface consists of 5-fold coordinated titanium (Ti_{5c}) atoms, in-plane oxygen atoms, and bridging oxygen atoms (Ob), 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 TiO₂(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 Ag₇O₈NO₃ 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 Ag₇O₈NO₃ crystals, on a rectangular lattice. However, the tetragonal TiO₂(110) surface has strong in-plane anisotropy, allowing the (111)-oriented Ag7O8NO3 crystals to grow epitaxially with only moderate in-plane mismatch.

3.3. Reaction selectivity against O₂ by-products

The effect of the electrode potential on the growth of $Ag_7O_8NO_3$ crystals on $TiO_2(110)$ was investigated. Fig. 5 shows the relative selectivity for the formation of $Ag_7O_8NO_3$ (filled circles) as a function of the electrode potential, together with SEM images of crystals grown at electrode



Fig. 5 (a) SEM images taken for samples grown at electrode potentials of (a) -0.15, (b) +0.2 and (c) +0.45 V, respectively. (d) Relative selectivity of the formation of Ag₇O₈NO₃ (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 $Ag_7O_8NO_3$ (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 TiO₂ 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 Ag₇O₈NO₃ 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 SrTiO₃(001) substrates, the clathrate formation selectivity actually increased at negative electrode potentials vs. Ag, although the absolute amount of deposited Ag₇O₈NO₃, of course, dropped in accordance with the decreasing total photocurrent. A strong electric field, on the order of 1 MV cm⁻¹, has been shown to occur at the interface between an electrode and an electrolyte.²⁴ Hot carriers that can be injected through quantized interface levels due to the strong electric fields²⁵ may be partly responsible for the observed electrode potential dependence.

3.4. Comparison of the growth behaviours of $Ag_7O_8NO_3$ and $Ag_7O_8HSO_4$ on Nb-doped TiO₂ single crystals

The photoelectrochemical synthesis of other types of silver oxide clathrates on Nb-doped TiO₂ single crystals was also studied under experimental conditions that were identical except for the composition of the electrolyte. Ag₇O₈HSO₄ crystals were successfully obtained in a 0.01 M Ag₂SO₄ solution, while the synthesis of Ag₇O₈ClO₄ in a 0.01 M AgClO₄ solution was possible, but the absolute amount was too small to be fully characterized. We therefore compare the growth of $Ag_7O_8HSO_4$ with $Ag_7O_8NO_3$. Fig. 6 shows a set of θ -2 θ XRD patterns of $Ag_7O_8HSO_4$ layers that were photoelectrochemically deposited in 2 hours on Nb-doped TiO₂ (110), (101), (100), and (001) single-crystal substrates in 0.01 M Ag₂SO₄ at an electrode potential of +0.3 V vs. Ag. The diffraction peak positions were very close to those of Ag₇O₈NO₃ because of the similar lattice constants (Ag₇O₈NO₃: 0.989 nm, $Ag_7O_8HSO_4$: 0.992 nm).⁷ No other peaks belonging to binary silver oxides or any other secondary phases could be detected. According to a Φ scan analysis (not shown), some Ag₇O₈HSO₄ crystals always grew epitaxially, regardless of the TiO₂ substrate orientation. The relative intensities of the Ag₇O₈HSO₄ XRD peaks were different from those of Ag₇O₈NO₃, which reflects a different out-of-plane orientation preference. The main difference was the presence of (100)-



Fig. 6 A set of θ -2 θ XRD patterns of photoelectrochemically deposited Ag₇O₈HSO₄ grown on Nb-doped TiO₂ (a) (110), (b) (101), (c) (100), and (d) (001) single-crystal in a 0.01 M Ag₇O₈HSO₄ solution at an electrode potential of +0.3 V vs. Ag in 2 h. All plots are shown on a logarithmic scale.

oriented grains in addition to the (111)-orientation, even on $TiO_2(110)$. A set of SEM images corresponding to the different substrate orientations are shown in Fig. 7. A comparison with the SEM images of $Ag_7O_8NO_3$ crystals in Fig. 2 clearly shows that the size and areal density of $Ag_7O_8HSO_4$ crystals are considerably larger than those of $Ag_7O_8NO_3$ on all TiO_2 crystal faces, but most remarkably on $TiO_2(110)$. However, it should be pointed out that since the concentration of Ag^+ ions in a 0.01 M Ag_2SO_4 solution is two times higher than that in a 0.01 M $Ag_7O_8HSO_4$ cannot be directly compared based on these two independent experiments if the growth rate depends on the concentration of Ag^+ in the solution.



Fig. 7 SEM images of the same set of $Ag_7O_8HSO_4$ samples for (a) (110), (b) (101), (c) (100), and (d) (001) single-crystal TiO₂ substrates that were used for the XRD analysis in Fig. 6.

In order to rule out this possibility, simultaneous photodeposition of $Ag_7O_8(MM')$ (M = NO₃, M' = HSO₄) on TiO₂(110) was tested by using mixtures of AgNO3 and Ag2SO4 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 crystallites were formed in a pure 0.01 M AgNO₃ solution after a 2-hour deposition. As the concentration of Ag_2SO_4 , $c_{Ag_3SO_4}$, in the mixed solution increased, the number of large crystals also increased, reaching a maximum size for $c_{Ag_2SO_4} = 0.01$ and decreasing for higher Ag₂SO₄ concentrations. It is noted that a very small, e.g. 20%, increase of Ag⁺ in the solution by adding Ag_2SO_4 ($c_{Ag_3SO_4}$ 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 Ag₇O₈NO₃ on Nb:SrTiO₃(001);¹² 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 $c_{Ag_3SO_4}$ should be proportional to the total amount of photodeposited silveroxide 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 $c_{Ag_2SO_4}$ 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 Ag₇O₈HSO₄ crystals can grow along the (100) direction on $TiO_2(110)$. We can therefore conclude that when mixtures of AgNO₃ and Ag₂SO₄ solutions are used under the present experimental conditions, the dominant (100)-oriented $Ag_7O_8(MM')$ phase is either pure $Ag_7O_8HSO_4$ or at least a Ag₇O₈HSO₄-rich mixed clathrate. The preferential formation of Ag₇O₈HSO₄ clathrate is probably caused by the faster growth rate of Ag₇O₈HSO₄ crystals when compared to $Ag_7O_8NO_3$ 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 Ag₇O₈HSO₄ is much smaller than that of $Ag_7O_8NO_3$ 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 Ag₇O₈NO₃ or Ag₇O₈NO₃-rich mixed clathrates as well as Ag₇O₈HSO₄, 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 AgNO3 and Ag2SO4 with different mixing ratios at an electrode potential of +0.3 V vs. Ag in 1 h.



Fig. 9 (a) EPMA intensity ratio of Ag/Ti as a function of the Ag₂SO₄ concentration in the photodeposition solution. The Ag/Ti ratio is proportional to the total amount of photodeposited silver oxide clathrate compounds. (b) Intensity ratio of the (400) and (222) XRD peaks. (c) EPMA S/Ag intensity ratio as a function of $c_{Ag_2SO_4}$.

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Furthermore, the decrease of the EPMA Ag/Ti intensity ratio, *i.e.*, the amount of $Ag_7O_8HSO_4$ or $Ag_7O_8HSO_4$ -rich mixed clathrates deposited as a major product, at $c_{Ag_2SO_4}$ higher than 0.01 M, can be understood when considering the very narrow Ag^+ ion concentration window of less than 0.005 M where $Ag_7O_8HSO_4$ can be synthesized by electrochemical oxidation.²

In simultaneous photodeposition of $Ag_7O_8(MM')$ (M = NO_3 , M' = HSO_4) the process that forms Ag_6O_8 cages through the oxidation of Ag^+ ions is common for both materials and the rate-limiting step for the growth of silver oxide clathrate Ag_7O_8M 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 Ag_6O_8 cages are responsible for the observed differences in the $Ag_7O_8NO_3$ and $Ag_7O_8HSO_4$ growth rates.

4. Conclusion

We have succeeded in photoelectrochemically synthesizing silver oxide clathrate Ag_7O_8M (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 Ag₇O₈NO₃ occurring on TiO₂(110). This result has confirmed that commensurate, epitaxial lattice matching can occur between a singlecrystal substrate lattice and the pseudo lattice of cages in an inorganic compound, such as the Ag₇O₈NO₃ 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 Ag₇O₈NO₃ over other by-products. It was found that the process of incorporating monovalent anions, such as NO_3^- or HSO_4^- , into the Ag_6O_8 cages is the likely rate-limiting step in this photoelectrochemical silver oxide clathrate synthesis, leading to different growth rates of Ag₇O₈NO₃ and Ag₇O₈HSO₄.

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