AIP | Applied Physics Letters

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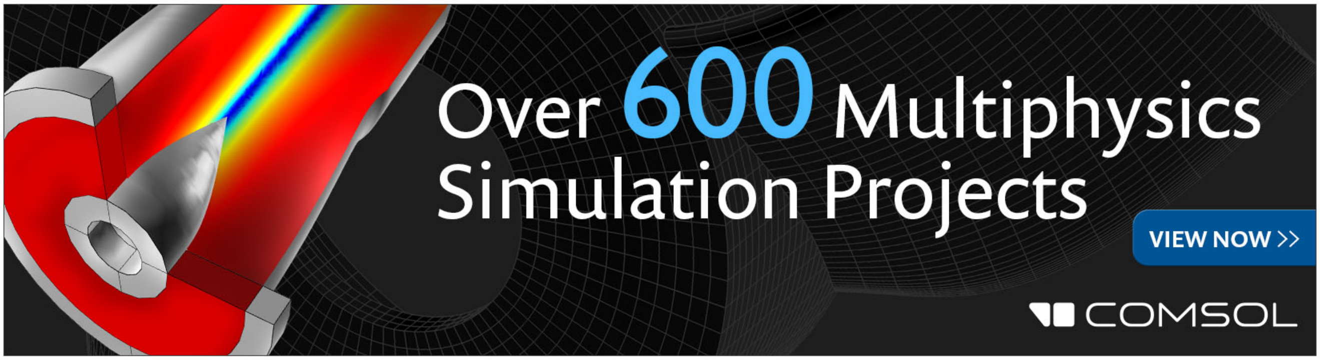
Citation: Applied Physics Letters **68**, 137 (1996); doi: 10.1063/1.116781
View online: http://dx.doi.org/10.1063/1.116781
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/68/1?ver=pdfcov
Published by the AIP Publishing



Room-temperature preparation of crystallized luminescent $Sr_{1-x}Ca_xWO_4$ solid-solution films by an electrochemical method

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(Received 9 August 1995; accepted for publication 20 October 1995)

A complete series of well-crystallized solid-solution oxide films, $Sr_{1-X}Ca_XWO_4$ ($0 \leqslant X \leqslant 1$), has been prepared on a tungsten substrate in the electrolytic solution containing Sr^{2+} and Ca^{2+} ions by an electrochemical method at room temperature (25 °C). The composition of solid-solution oxide films could easily be controlled by the concentrations of Sr and Ca species in the starting solutions. The films showed only single blue emission at liquid nitrogen temperature (−196 °C), strongly suggesting that they consisted of well-crystallized defect-free crystals. *© 1996 American Institute of Physics.* [S0003-6951(96)01101-3]

Scheelite-type alkaline earth tungstates have been extensively investigated since they have been proven to be good laser host materials.[1–8] Their films are more important for better performance in industrial applications. In order to fully realize the potential of the films, it is necessary to synthesize the solid-solution films and to investigate systematically their physical properties such as luminescence, lattice parameters, and so on, because the composition of the solid solution affects such physical properties. Nevertheless, even for $CaWO_4$, only limited investigations have been performed on the preparation of the film.[9,10] Some problems remain in these studies.[9,10] $CaWO_4$ films[9] prepared by sputtering contained impurity phases such as Ca_3WO_6, Ca_6WO_9, WO_3, and $WO_3 \cdot 0.33H_2O$ because of the high vapor pressure of WO_3. $CaWO_4$ films[10] prepared by the vacuum evaporation showed no luminescence because of their poor crystallinity. In order to increase the crystallinity of the films, heat treatments (500 to 1100 °C) were necessary. This led to cracking and/or peeling of the film due to shrinkage during crystallization and/or thermal treatment. These problems make the preparation of solid-solution films more difficult.

Recently, electrodeposition methods have been thought to have potential for the economical production of thin films because they require simple instrumentation and can produce large-area films. While most of the studies so far have been restricted to the electrodeposition of a single oxide or a double oxide, the deposition of defined solid-solution films has been the subject of only a few investigations.[11,12] All components of the oxides were codeposited on the electrode from the solution during the electrochemical treatments. In these previous works, as-deposited films were amorphous; therefore, an additional heat treatment (400–1000 °C) was necessary for their crystallization. Moreover, impurity phases existed in these films. To our knowledge, there have been no reports on a complete series of well-crystallized solid-solution oxide films at room temperature. On the other hand, our research effort has been devoted to low-temperature preparation of crystalline oxide films directly from solutions without firing or heat treatments after/during film shaping.[13–15] Our work in a previous letter[15] has confirmed the synthesis of $CaWO_4$ by electrochemically reacting a tungsten substrate with alkaline $Ca(OH)_2$ solution at room temperature (25 °C). In the $CaWO_4$ preparation, a growth model has been proposed as follows:[15]

$$W + 4H_2O \rightarrow WO_4^{2-} + 8H^+ + 6e^-, \tag{1}$$

$$WO_4^{2-} + Ca^{2+} \rightarrow CaWO_4. \tag{2}$$

In alkaline solution containing both Ca and Sr species, solid-solution films of $Sr_{1-X}Ca_XWO_4$ could be prepared as follows:

$$WO_4^{2-} + (1-X)Sr^{2+} + XCa^{2+} \rightarrow Sr_{1-X}Ca_XWO_4. \tag{3}$$

The synthesis of solid-solution films with multicomponents has more significant meaning for the general applicability of this film technique. In the present study, we describe the successful synthesis of luminescent crystallized $Sr_{1-X}Ca_XWO_4$ ($0 \leqslant X \leqslant 1$) solid-solution films at room temperature.

Tungsten metal substrates with 99.9 wt % in purity and dimensions of 10×40×0.2 mm were used as counterelectrode (i.e., cathode) and working electrode (i.e., anode). Prior to the electrochemical treatment, the tungsten substrates were degreased in acetone with an ultrasonic cleaner. Elec-

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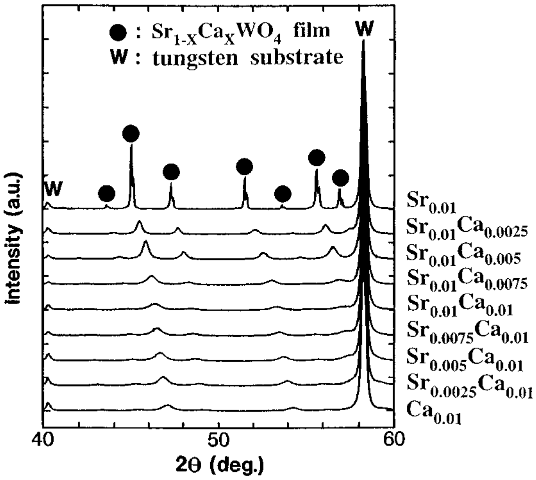

FIG. 1. X-ray diffraction patterns of the $Sr_{1-X}Ca_XWO_4$ films prepared on the anodic tungsten substrates by the electrochemical treatment. The compositional formula Sr_xCa_y denotes the concentrations in the starting mixed solution: xM for Sr and yM for Ca.

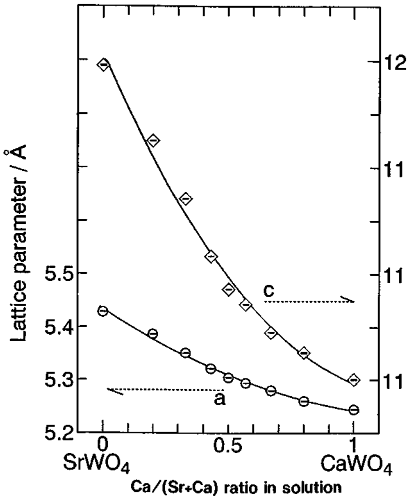

FIG. 2. Variation of the lattice parameters of the $Sr_{1-X}Ca_XWO_4$ films with the Ca/(Sr+Ca) ratio of the starting solution.

trolytic solutions were prepared by preheating the redistilled water to remove dissolved CO_2 and then adding $Sr(OH)_2 \cdot 8H_2O$ and $Ca(OH)_2$ with a purity of 96.0 wt. %. All experiments were performed with stirring of 200 rpm at room temperature (25 °C) under galvanostatic conditions (i.e., constant current) with a current density of 1 mA/cm^2 generated by a commercial power source (Type PAD 1K-0.2L, Kikusui Electronics Co.). The microstructures of the films were investigated by scanning electron microscopy (JSM-T200, JEOL). The phases thus obtained were analyzed by x-ray diffractometry (MXP^{3VA}, Cu $K\alpha$, graphite monochrometer, 40 kV–40 mA, MAC Science). Raman spectroscopy (T64000, Atago-Jobin Yvon) was also employed to investigate the existing phase and the homogeneity of the prepared film. Raman spectra were excited with a 514.5 nm line of an argon ion laser using a micro-Raman system (spot size $\sim 1 \mu$m). Luminescence spectra were measured using a spectrofluorometer (Fluoromax™, Spex) at liquid nitrogen temperature (−196 °C). The composition of the film prepared in a solution with a Ca/(Ca+Sr) ratio of 0.5 was confirmed by x-ray photoelectron spectroscopy (ESCA-850, Shimadzu).

Figure 1 shows the x-ray diffraction patterns of $Sr_{1-X}Ca_XWO_4$ ($0 \leqslant X \leqslant 1$) films prepared on the tungsten substrates by the electrochemical treatment. Each peak of the $Sr_{1-X}Ca_XWO_4$ film shifted to a higher 2θ position with an increase of Ca concentration of the starting aqueous solution, although the peak positions of the tungsten substrate were almost unchanged. The unit-cell parameters of tetragonal $Sr_{1-X}Ca_XWO_4$ changed continuously with the Ca/(Ca+Sr) ratio in solution from $a=5.428$ Å, $c=11.989$ Å for $X=0$ to $a=5.245$ Å, $c=11.399$ Å for $X=1$ (Fig. 2). These values for $X=0$ and 1 agree well with those in the literature.[16,17] The composition of film prepared in a solution of 0.01 M $Ca(OH)_2$ and 0.01 M $Sr(OH)_2 \cdot 8H_2O$ has been investigated by both the unit-cell parameter and x-ray photoelectron spectroscopy. The composition ($Sr_{0.33}Ca_{0.67}WO_4$ from the a axis, $Sr_{0.31}Ca_{0.69}WO_4$ from the c axis) calculated from the unit-cell parameters agrees with that ($Sr_{0.36}Ca_{0.64}WO_4$) obtained by x-ray photoelectron spectroscopy. These results indicate that crystallized solid solutions form in the whole compositional range ($0 \leqslant X \leqslant 1$) and that their compositions are controlled by the concentrations of the starting solutions. The x-ray diffraction patterns also show a large decrease in peak intensities and a large increase in full width at half maximum (FWHM) of peaks going from the Sr to the Ca tungstate while the intensity and FWHM of the tungsten substrate remain about the same. The decrease in peak intensities is due to both a decrease in the film thickness and the difference of atomic scattering factor[18] between Ca [14.32 for $(\sin \theta)/\lambda = 0.2$ Å^{-1}] and Sr [29.83 for $(\sin \theta)/\lambda = 0.2$ Å^{-1}]. Scanning electron micrographs showed the decrease of film thickness from about 6 μm for $SrWO_4$ to about 3 μm for $CaWO_4$. The peak broadening with increasing of the Ca/(Sr+Ca) ratio in the solution is ascribed to a decrease in crystallite size. The crystallite size has been estimated using Scherrer's formula from the FWHM values of the 100 and 001 reflections. The size

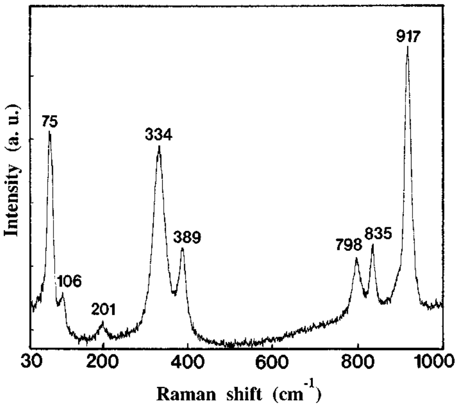

FIG. 3. Raman spectrum of film prepared on the anodic tungsten substrate by the electrochemical treatment of 4.5 h at room temperature in the mixed solution of $Sr(OH)_2 \cdot 8H_2O$ and $Ca(OH)_2$ of 0.01 M, respectively. Each number denotes the Raman shift of a peak top.

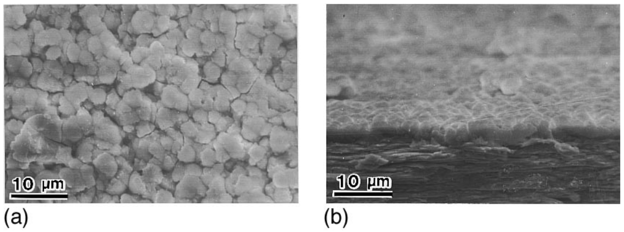

FIG. 4. Scanning electron micrographs of the surface (a) and cross section (b) of $Sr_{1-X}Ca_XWO_4$ film prepared on an anodic tungsten substrate at room temperature in the mixed solution of $Sr(OH)_2 \cdot 8H_2O$ and $Ca(OH)_2$ of 0.01 M, respectively.

decreased with an increase of the Ca/(Sr+Ca) ratio in the solution. For $CaWO_4$ film, the values were about 15 nm from a 100 reflection and about 55 nm from a 001 reflection, which agree with the average size (about 40 nm) observed by scanning electron microscopy. A typical Raman spectrum of the $Sr_{1-X}Ca_XWO_4$ film is shown in Fig. 3. All samples exhibited Raman spectra of the tetragonal scheelite-type structure[19] without any impurity phases. Scanning electron micrographs in Fig. 4 show the surface and cross section of the $Sr_{1-X}Ca_XWO_4$ solid-solution film. The grain size is larger than the film thickness. This means that the initially formed crystals grow preferentially in the horizontal direction of the substrate, which provides a better supply of the tungsten species. As shown in Fig. 5, the important feature is that the films exhibited only a blue emission. Such a single luminescent feature strongly suggests that the films are defect-free.[20,21] Grasser and Scharmann observed a green emission in addition to the blue emission at liquid nitrogen temperature (−196 °C) in the alkaline earth tungstates with a scheelite-type structure that contained defects. This green emission was interpreted to be ascribed to the existence of Schottky-defect WO_3.[21] In the present film, such green emission was not observed, but there existed only single blue emission. The peak positions of the excitation and emission of the $Sr_{1-X}Ca_XWO_4$ solid-solution films were independent of the Ca content: 250±2 nm for excitation and 463±2 nm for emission. Almost all the researchers working in this field have shared the opinion that the blue band in $CaWO_4$ is due to an electron transition within undisturbed WO_4^{2-} complexes.[22] Our results suggest that the energy gap related to the blue emission in WO_4^{2-} complexes is almost unaffected by the change in Ca content. However, there were variations in the intensities of the emissions: The films in the Ca-rich region showed an extremely strong luminescence, while the films in the Sr-rich region showed a much fainter emission. A theoretical approach is necessary for a successful interpretation of the optical properties of these films. However, theoretical band calculations have not been carried out yet, due to the fact that these solids have a large number of atoms in the unit cell.[22]

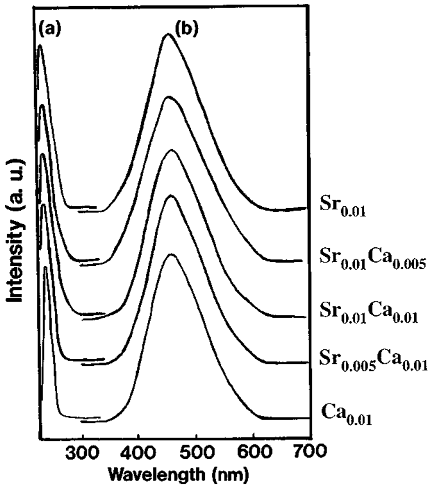

FIG. 5. Excitation (a) and emission (b) spectra of the $Sr_{1-X}Ca_XWO_4$ films at liquid nitrogen temperature. The intensities of the spectra were normalized. The compositional formula Sr_xCa_y denotes the concentrations in the starting mixed solution: xM for Sr and yM for Ca.

It is rather surprising that a complete series of crystallized $Sr_{1-X}Ca_xWO_4$ $(0 \leqslant x \leqslant 1)$ solid-solution films can be formed even at room temperature (25 °C). Furthermore, it is noteworthy that the present films are defect-free showing a single blue emission and do not contain any impurity phases, contrary to the films prepared by sputtering at higher temperatures.

This work was supported by a Grant-in-Aid for Scientific Research No. 07405028, NEDO International Joint Research Grant. The authors would like to thank M. Osada for help with Raman spectroscopy, and M. Ishiyama for assistance with x-ray photoelectron spectroscopy.

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