Novel solid-phase epitaxy for multi-component materials with extremely high vapor pressure elements: An application to KFe$_2$As$_2$

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Received March 11, 2016; accepted March 23, 2016; published online April 8, 2016

We propose a novel solid-phase epitaxy technique applicable to high annealing temperatures up to 1000 °C without re-vaporization of alkali metal elements with high vapor pressures. This technique is demonstrated through the successful growth of high-quality KFe$_2$As$_2$ epitaxial films. The key factors are employing a custom-designed alumina vessel/cover and sealing it in a stainless tube with a large amount of atmospheric KFe$_2$As$_2$ powder in tightly closed sample spaces. This technique can also be effective for other materials composed of elements with very high vapor pressures, such as alkali metals, and can lead to the realization of spintronics devices in the future using KFe$_2$As$_2$.

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All of the XRD measurements were performed using an O-ring sealed sample carrier filled with dry Ar gas to prevent degradation of the samples during measurements.

Figure 1 summarizes the newly developed solid-phase epitaxy process for materials composed of alkali metals with high vapor pressures. At first, an amorphous KFe$_2$As$_2$ layer was deposited on an MgO substrate by PLD using the K-rich KFe$_2$As$_2$ target, as reported in Ref. 7 [Fig. 1(a)]. The resulting film was then transferred directly from the PLD preparation chamber to a dry and inert glove box, and covered with a fresh MgO plate [Fig. 1(b)]. The film was tightly covered with a large amount of stoichiometric KFe$_2$As$_2$ powder in a custom-designed alumina vessel, in order to compensate the high vapor pressure of K during the high temperature annealing process at 1000 °C. The capping MgO plate is effective in preventing evaporation of the film constituents during thermal annealing as well as chemical reaction between the film surface and covering KFe$_2$As$_2$ powder. The alumina vessel has two deep spaces with a lateral size of 10.2 × 10.2 mm$^2$ (i.e., almost the same lateral size as that of the MgO substrate) and a depth of 5 mm to fill sufficient KFe$_2$As$_2$ powder. Then the alumina vessel was covered with a custom-made alumina cover. Both sides of the vessel and the cover were tightly clenched by commercially available bolts and nuts made of alumina to keep it gas-tight around the samples during high temperature thermal annealing. The tightly sealed alumina vessel was set in an Ar-filled stainless tube, both ends of which are sealed by stainless nuts and gaskets to keep it gas-tight. From (a) to (b), the sample is transferred directly from the preparation chamber of PLD (vacuum) to the glove box in pure Ar with a dew point of ca. −100 °C. The process in (b) is performed in the glove box. (c) Thermal annealing process in an electric furnace at 1000 °C (left). Then the stainless tube is transferred to the glove box, and cut open by a tube cutter to pick out the sample (right photographs). The sample is not exposed to air throughout the whole process.

Fig. 1. Schematic of the experimental setup for a newly developed solid-phase epitaxy for growing KFe$_2$As$_2$ epitaxial films, via a post-deposition thermal annealing process. (a) Film-deposition process by PLD at room temperature (RT). (b) Setup before thermal annealing. The surface of the as-deposited amorphous film is covered with a fresh MgO substrate. The film is then transferred to a custom-designed alumina vessel with small sample spaces. The films (maximum two samples) are covered with a large amount of stoichiometric KFe$_2$As$_2$ powder. Then the alumina vessel is tightly covered with a custom-designed alumina cover with commercially available bolts and nuts made of alumina to keep it gas-tight around the samples during high temperature thermal annealing. The tightly sealed alumina vessel is set in an Ar-filled stainless tube, both ends of which are sealed by stainless nuts and gaskets to keep it gas-tight. Both sides of the vessel and the cover were tightly clenched by commercially available bolts and nuts made of alumina. The drawings of the custom-designed alumina vessel and cover are shown in Fig. S1 in the online supplementary data at http://stacks.iop.org/APEX/9/055505/mmedia. This tightly sealed alumina vessel was set in a stainless tube filled with dry Ar. Both ends of the stainless tube were tightly clenched by stainless nuts and gaskets to keep it gas-tight during high temperature annealing. In the previous study, we employed a silica-glass tube to keep the sample and vessel in an evacuated atmosphere. This method required a high temperature heating process to seal the glass tube while keeping the sample at lower temperatures (close to room temperature), which was technically difficult. In the
present process, however, we can easily perform the sealing in a glove box without heating. The present technique does not require any special experimental skills and can be performed by anyone and applicable for any materials that will easily decompose or react when heated. All the processes in Fig. 1(b) were performed in a dry and inert glove box. This tight sealing method prevents vaporization of K during high temperature annealing even at 1000 °C for 30 min [Fig. 1(c) left]. The maximum available temperature by this technique is 1000 °C, because annealing at above 1000 °C causes a re-vaporization of K, similar to the previously reported technique at 800 °C in Ref.7. After annealing using the present technique, the stainless nuts were sintered to the stainless tube and could not be loosened. Thus, we cut open the tube by a tube cutter and then picked out the sample in the glove box [see Fig. 1(c), right photograph].

Figure 2 shows the XRD patterns of the KFe$_2$As$_2$ films grown at 1000 °C through a newly developed solid-phase epitaxy technique. The out-of-plane $\omega$-coupled 20 synchronous scan pattern [Fig. 2(a)] indicates that the obtained films are strongly c-axis oriented. The full width at half maximum (FWHM) of the 002 diffraction rocking curve [Fig. 2(b)] is 0.06°, which is nearly one order smaller than that obtained using the previous technique (0.4°). Figure 2(c) shows the in-plane $\phi$-coupled 20$\gamma$ synchronous scan pattern, indicating that the films are oriented in-plane as well as out-of-plane. Because the $\alpha$-axis lattice parameter of the film is close to that of MgO, the peaks from the KFe$_2$As$_2$ film and MgO substrate could not be resolved. Therefore, we performed pole figure measurements of the asymmetric 103 diffraction [see Fig. 2(d)] to confirm the in-plane symmetry of the film. We observed a clear four-fold symmetric diffraction due to the tetragonal symmetry of KFe$_2$As$_2$ at $\Psi = 50^\circ$ and every $\phi = 90^\circ$. These results indicate that the KFe$_2$As$_2$ films grew heteroepitaxially on MgO(001) single-crystal substrates with an epitaxial relationship: [001] KFe$_2$As$_2$ || [001] MgO for out-of-plane and [100] KFe$_2$As$_2$ || [100] MgO for in-plane. This result is significantly different from that of the previous study, in which c-axis oriented films were obtained but a clear in-plane heteroepitaxy was not observed, due to the limitation of a maximum annealing temperature of 700 °C. The estimated lattice parameters of the as grown KFe$_2$As$_2$ film are $a = 0.3924$ and $c = 1.374$ nm. This result indicates that the c-axis of the film slightly shrinks (~1%) while its $\alpha$-axis slightly expands (+2%), compared to those of the bulk ($c = 1.384$ nm, $a = 0.3841$ nm, Ref. 2), probably due to a relatively large in-plane lattice mismatch between KFe$_2$As$_2$ and MgO (+9%).

In conclusion, we developed a new solid-phase epitaxy technique to grow high-quality epitaxial films of compounds composed of alkali metals. It was demonstrated that for the KFe$_2$As$_2$ epitaxial films, the out-of-plane rocking curve width was decreased by an order of magnitude compared to previous results, and the in-plane XRD pattern completely overlapped with that of the MgO substrate. Since KFe$_2$As$_2$ is very air-sensitive and incompatible with conventional lithography techniques, we could not measure its SHC, which, however, can be achieved by developing a nanometer-size patterning technique for such highly air-sensitive materials. The solid-phase epitaxy technique employs a custom-designed alumina vessel and a sealing in Ar-filled stainless tube with a large amount of atmospheric powder (e.g., KFe$_2$As$_2$). This technique is a powerful tool for growing high-quality thin films composed of high vapor pressure elements.

Acknowledgments This work was supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) through Element Strategy Initiative to Form Core Research Center. H.Hi. was also supported by the Japan Society for the Promotion of Science (JSPS) Grant-in-Aid for Young Scientists (A) Grant Number 25700058, JSPS Grant-in-Aid for Scientific Research on Innovative Areas “Nano Informatics” (Grant Number 25106007), and Support for Tokyotech Advanced Research (STAR).

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