Effect of Sr doping on structure, morphology and transport properties of Bi$_2$Se$_3$ epitaxial thin films

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We report molecular beam epitaxy growth of Sr-doped Bi$_2$Se$_3$ films on (111) BaF$_2$ substrate, aimed to realize unusual superconducting properties inherent to Sr$_x$Bi$_2$Se$_3$ single crystals. Despite wide range of the compositions, we do not achieve superconductivity. To explore the reason for that we study structural, morphological and electronic properties of the films and compare them to the corresponding properties of the single crystals. The dependence of the c-lattice constant in the films on Sr content appears to be more than an order of magnitude stronger than in the crystals. Correspondingly, all other properties also differ substantially, indicating that Sr atoms get different positions in lattices. We argue that these structural discrepancies come from essential differences in growth conditions. Our research calls for more detailed structural studies and novel growth approaches for design of superconducting Sr$_x$Bi$_2$Se$_3$ thin films.

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INTRODUCTION

In past decade three-dimensional topological insulators (3D TI) gain a lot of interest. This kind of quantum materials has insulating bulk and topologically protected conducting surfaces with spin-momentum locking, and, hence nontrivial electrodynamical properties. Classical layered thermoelectric materials Bi$_2$Se$_3$ and Bi$_2$Te$_3$ appeared to be the most explored among variety of 3D TIs due to well developed technology of synthesis and wide band gap.

Introduction of Cu, Sr, Nb was found to make bismuth selenide superconducting$^{[1,2]}$. This superconductivity is attractive both from fundamental point of view (as its mechanism and possible topological nature are not explored yet) and for applications (i.e. the platform for future quantum computations if the superconductivity is topological). However, all experimental observations of superconductivity in these materials so far were restricted to bulk single crystals.

Evidently, for any practical applications, scalable thin-films based technology is required, rather than exfoliation of thin single crystalline flakes. Molecular beam epitaxy of parent material Bi$_2$Se$_3$ on various substrates was developed in past few years$^{[2]}$; record mobilities of $\sim 16000$ cm$^2$/Vs were achieved$^{[2]}$, and possibility of Fermi level tuning both by gate and by doping were demonstrated$^{[7]}$. Apparently, the growth of superconducting M$_x$Bi$_2$Se$_3$(where M = Cu, Sr, Nb) thin films would be a future great achievement in technology of these topological materials.

As superconductivity was first discovered in the Cu$_x$Bi$_2$Se$_3$ crystals in 2010$^{[8]}$, thin films with the same dopant were also grown soon$^{[9,11]}$, and turned out to be non superconductive. Surprisingly, instead of increase of carrier density, the epitaxial Cu-doped films even demonstrated a tendency to insulating behavior$^{[12]}$. Bulk Sr$_x$Bi$_2$Se$_3$, discovered in 2015$^{[13]}$, seems to be more prospective than Cu-doped Bi$_2$Se$_3$, as Sr-doped material is air-stable and demonstrates almost 100% superconductive volume$^{[14-16]}$. In addition, the bulk carrier density in Sr$_x$Bi$_2$Se$_3$ ($\sim 2 \cdot 10^{19}$ cm$^{-3}$) is an order of magnitude smaller than in Cu$_x$Bi$_2$Se$_3$. Such low density for ultrathin ($\sim 10$ nm) film would provide 2D carrier density per unit area as small as $2 \cdot 10^{13}$ cm$^{-2}$. It opens a way for switching superconductivity using routinely available field effect transistor structure.

To the best of our knowledge, epitaxial Sr-doped Bi$_2$Se$_3$ films were reported in papers two times$^{[8,17]}$. Ref.$^{[17]}$ presents only two films with $x = 0.05, 0.13$ and concentrates on micro structural properties (searching for Sr atoms positions). In Ref.$^{[7]}$, devoted to (Ca$_{x}$Bi$_{1-x}$)$_2$Se$_3$ system, several Sr-doped films with $x \leq 1\%$ are mentioned in supplementary. Thus, the systematic study of growth process and its correlation with structural and transport properties is lacking. Our research aims to fulfill this gap.

We report epitaxial growth, detailed structural, and low-temperature magnetotransport studies of Sr-doped Bi$_2$Se$_3$ thin films on BaF$_2$ substrate. Despite the wide range of growth parameters, the superconductivity was not achieved. In order to find out the possible reason for that we compared structural properties of superconducting bulk crystals and thin films. We observe essential enhancement of the c-axis parameters with $x$ in the films compared to that in bulk crystals. Morphology and transport studies suggest that Sr introduces disorder to the films. Our data thus indicate that Sr atoms in films and bulk crystals take different positions in the lattices. The position of Sr atoms is therefore decisive for superconductivity.
GROWTH AND STRUCTURAL CHARACTERIZATION TECHNIQUES

Growth technique

Growth of Sr-doped Bi$_2$Se$_3$ films on cleaved (111) BaF$_2$ substrates was performed in a MBE system EP-1201 with a pressure 3·10$^{-10}$ Torr during epitaxy [13,14]. Ternary Sr$_2$Bi$_2$-xSe$_3$ layers were deposited using standard effusion cells for high purity elemental Se, Sr and binary Bi$_2$Se$_3$ compound. Atomic/molecular fluxes were calibrated using Bayard-Alpert ion gauge that swings into the substrate position. Stability of the beam equivalent pressure (BEP) for each cell was controlled just before starting the deposition and immediately after the growth finish. The cells temperatures for Se (130°C) and Bi$_2$Se$_3$ (495°C) were held constant, that resulted in Se-rich conditions with a BEP flux ratio Se/Bi$_2$Se$_3$ of 2:1 and provided layer growth rate of 0.25 nm/min. Thin films with different Sr content were obtained by varying the evaporation temperature of the Sr effusion cell. Sr concentration $x$ in the grown films was increased from 0.003 to 0.352 when heating Sr cell from 260 to 380°C. Growth of the film was started at 260°C with opening Se and Bi$_2$Se$_3$ cell shutters. Following the 4 minute deposition of the first quintuple layer (QL) of binary Bi$_2$Se$_3$, substrate temperature was ramped up to 300°C in the next 4 minutes without growth interruption. Then Sr cell shutter was opened for the deposition of the body of the ternary film on top of the 2QL thick buffer layer. Thin films with different Sr composition $x$ and thicknesses of 20-50 nm were obtained by the described approach. Immediately after the growth, the film on the substrate was cooled down to room temperature. Then, an amorphous 30 nm thick Se cap layer was deposited in order to protect the film surface from ambient atmosphere. Concentration $x$ of Sr in the Sr$_2$Bi$_2$-xSe$_3$ layers was deduced from the growth rates of the bare Bi$_2$Se$_3$ and SrSe reference layers, grown on (111) BaF$_2$ substrates. A series of Sr$_2$Bi$_2$Se$_3$ bulk crystals with nominal Sr content of $x$=0, 0.01, 0.037 and 0.15 were prepared using modified Bridgeman method [15]. To compare properties of thin films and bulk crystals, within this paper we define nominal composition $x$ as a molar fraction of dopant $x$ times 100% (below we will give nominal $x$ in percentage).

X-ray measurements

The X-ray diffraction(XRD) and X-ray reflection(XRR) measurements were carried out on Panalytical MRD Extended diffractometer with a hybrid monochromator, that is a combination of a parabolic mirror and a single crystal 2×Ge(2 2 0) monochromator. We used triple crystal-analyzer 3×Ge(2 2 0) to get high resolution ($2\theta - \omega$)-scanning curves for lattice parameter determinations. Thickness of the films was obtained from (006) Bragg peak diffraction fringes and/or from X-ray reflection (XRR) spectra.

FIG. 1: a) Schematics of electrical connections used in transport measurements. b) Image of sample. The arrows show the geometrical definition of width and length.

Atomic force microscopy measurements

The morphology of the representative films was explored using the atomic force microscopy (AFM). For these measurements selenium capping layer was removed by annealing a sample in a vacuum at 200°C for 10 minutes. The measurements were performed using NT-MDT Solver 47 Pro system in tapping mode at ambient conditions.

Transport measurements

Hall-bar film geometries for transport measurements were defined by scratching the films with needle, similarly to Ref.[18]. Samples were mounted on the holder and contact wires were attached with silver paint (contact resistance was typically below several hundreds Ohms). Geometrical factor $l/w$ for every sample was evaluated from the camera image of the Hall bar, as shown in Fig. 1b. Low-temperature magnetotransport measurements were performed using a standard lock-in technique at frequencies 13 – 80 Hz and measurement current 1 µA to ensure the absence of overheating at the lowest temperatures. All measurements were performed in the temperature range 1.6 K-300 K using Cryogenics dry CFMS-16 system. Perpendicular magnetic field was swept (typically at 2,4,8,16,32 K) from positive to negative value(typically 1T). In order to compensate contact
misalignment, the magnetoresistance (Hall resistance) data were symmetrized (antisymmetrized). Using the $p_{xx}(B)$ and $p_{xy}(B)$ dependencies we determined the carrier density, Hall mobility and investigated weak antilocalization. The main structural and transport parameters are summarized in Table I and discussed below in Results and Discussion sections.

**EXPERIMENTAL RESULTS**

Structural and morphological results

In Fig. 2 diffractograms ($2\theta - \omega$)-scans of four representative samples with different Sr composition (listed in Table I) are shown. Besides the intensive (1 1 1), (2 2 2) reflections from BaF$_2$ substrate (partially cut for better visibility of the film signal) a series of (00.1) reflections from the film are clearly seen. They evidence for the growth of highly oriented layers with basal plane (00.1) parallel to the BaF$_2$ substrate (1 1 1) cleavage plane. As Sr content $x$ rises from $x = 0$% to $x = 14\%$, the (00.1) peaks get wider, indicating the increase of structural disorder (see columns $\Delta \omega_{0.06}$, $\Delta \omega_{0.015}$ of Table I). At the same time, the reflections with $l \leq 15$ shift to smaller diffraction angles. For $x \approx 25.8\%$ in addition to broadening, the (00.6) and (00.15) reflections split, while the intensities of (00.9) and (00.12) ones get suppressed. Thus, $x=25.8\%$ sample already consists of crystallites with different Sr composition, and film becomes inhomogeneous.

High resolution ($2\theta - \omega$) scans of (00.6) reflection are shown in Fig. 3. The peak position is clearly seen to move to smaller angles with $x$, indicating that $c$-lattice parameter substantially grows as doping level increases from 0% to 14%. Coming back to Fig. 2 one can see that for $x > 13\%$, the (00.18) and (00.21) reflections are shifted to the opposite direction (high $\theta$ values). This observation might be due to decrease of the XRD intensity from the defective highly Sr-doped fragments of the films.

For low Sr doping level (below 4%) we observe intensity fringes near the central (00.6) peak (see Fig. 3). Their period straightforwardly gives the film thickness $d \approx \frac{\lambda}{\Delta \omega_{0.06}}$, where $\omega_1$ and $\omega_2$ are neighboring maxima positions, and $\lambda$ is a X-ray wavelength. Intensity of the main reflection and its satellites decreases with $x$. Satellites are fully smeared by structural disorder for doping levels above 4%.

![X-ray diffraction scans](image)

**FIG. 2: X-ray diffraction scans** for epitaxial films with different Sr content $x$ (in %, from bottom to top), specified by different colors: 0% - black, 1.8% - red, 14% - blue, and 25.8% - green.

Fig. 4 shows the doping level dependence of the $c$-lattice parameter determined from both (00.6) and (00.15) reflections. There is a very small difference between $c_{0.06}$ and $c_{0.015}$ for $x$ below 12%. Above $x = 12\%$ the $c_{0.06}$ and $c_{0.015}$ values start to differ dramatically, that indicates that above 12% crystal structure becomes

| Sample | $X_{Sr}$ (%) | d (nm) | Parameters $c_{00.6}, c_{00.15}, a_{01.5}$ | RRR | $n$ (cm$^{-2}$) | $\mu$ (cm$^2$/Vs) | $\Delta \omega_{0.06}$ | $\Delta \omega_{0.015}$ | $\Delta c/c$ |
|--------|---------------|--------|------------------------------------------|-----|----------------|-----------------|----------------|----------------|-------------|
| 771    | 0             | 25.4   | $c_{00.6}=28.710, c_{00.15}=28.724, a_{01.5}=4.1305$ | 1.53 | $3.1 \cdot 10^{13}$ | 1400            | 0.158           | 0.199           | 0.049        |
| 763    | 0.3           | 25.9   | $c_{00.6}=28.706, c_{00.15}=28.722, a_{01.5}=4.129$ | 1.51 | $1.5 \cdot 10^{13}$ | 2989            | 0.165           | 0.229           | 0.056        |
| 762    | 0.8           | 30.7   | $c_{00.6}=28.754, c_{00.15}=28.764, a_{01.5}=4.125$ | 1.48 | $1.0 \cdot 10^{13}$ | 800             | 0.214           | 0.279           | 0.035        |
| 757    | 1.8           | 24     | $c_{00.6}=28.811, c_{00.15}=28.822, a_{01.5}=4.125$ | 1.64 | $4.7 \cdot 10^{13}$ | 681             | 0.171           | 0.239           | 0.038        |
| 747    | 3.6           | 24     | $c_{00.6}=28.805, c_{00.15}=28.824, a_{01.5}=4.126$ | 1.50 | $9.7 \cdot 10^{13}$ | 389             | 0.190           | 0.41            | 0.066        |
| 746    | 10.5          | 24     | $c_{00.6}=28.956, c_{00.15}=28.936, a_{01.5}=4.117$ | 1.43 | $8.9 \cdot 10^{13}$ | 142             | 0.320           | 0.46            | 0.069        |
| 778    | 15.7          | 29.2   | $c_{00.6}=29.073, c_{00.15}=28.879, a_{01.5}=4.115$ | 1.4  | $2.0 \cdot 10^{13}$ | 120             | 0.658           | 0.868           | -0.67        |
| 745    | 25.8          | 35.6   | $c_{00.6}=29.487, c_{00.15}=28.979$ | -    | -               | -               | -               | -              | -            |
| 748    | 35.2          | 25     | $c_{00.6}=28.714, c_{00.15}=29.927$ | 1.03 | $1.5 \cdot 10^{14}$ | 87              | -               | -              | -            |

**TABLE I: Summary of sample parameters.** The amount of Sr in Bi$_2$Se$_3$ films $X_{Sr}$ was calculated from the flow ratios. Thickness $d$ and parameters $a, c$ were determined from XRD. Carrier density($n$) and mobility ($\mu$) were obtained from low-field Hall measurements. Residual-resistivity ratio(RRR) was calculated as room temperature resistivity($R_{RT=300K}$) ratio to the minimum of resistivity in the low temperatures.
FIG. 3: 2θ − ω XRD scans on (0 0 6) reflex for films with different x content increasing from bottom to top, indicated in the panel.

more defective. The monotonic increase of c-parameter by approximately 1% with x (for x ≈ 12%) can be well interpolated by linear approximation with the slope $\frac{dc}{dx} = 2.05 \text{pm}/%$ (black line Fig. 4). Note, that for the bulk crystals (red dashed line) the slope is 10 times smaller, $\frac{dc}{dx} = 0.2 \text{pm}/%$. That strong c-axis increase with x indicates that Sr atoms predominantly substitute Bi atoms or occupy interstitial sites within quintuple-layer (QL), rather than intercalate into Van-der Waals (VdW) gap.

With that strong variation of c-lattice parameter accompanied by structural degradation we may expect a pronounced evolution of thin film morphology with composition. Fig. 5 shows the AFM (5 × 5 µm$^2$) scans of four representative 25 nm thick films with various Sr doping level. Undoped film demonstrates a rather big triangular domains with flat terraces and linear dimensions above 1 µm (RMS=0.64 nm). This domains have predominantly the same orientation (see Fig. 5a) reflecting a rather small twinning-level. The size of domains tends to decrease with x. In addition, concentration of twin domains substantially increases, as seen from Fig. 5b, c. An average domain size is 280 nm (RMS=0.61), and drops to 190 nm (RMS=0.97) for x=0.3% and 0.8%, respectively. For more heavily doped (10.5%) film, the in-plane triangular domain structure is not AFM resolved (see Fig. 5d). A rather similar morphological transformations were observed on doping Bi$_2$Se$_3$ with Ca [7].

Evolution of the film domain structure with x is clearly confirmed by XRD ϕ scans about of the [00.1] axis on asymmetric (1 0.10) reflection (see Fig. 6). Instead of 120° periodic reflections, as expected for trigonal crystal, we see peaks repeated every 60°. Ratio between amplitudes of two sets of peaks reflects twinning degree. In the undoped Bi$_2$Se$_3$ film, the intensity ratio of peaks for different 60°-twin domains is 6:1. In x ≈ 1.8% film this ratio drops to 1.7 : 1 and further tends to 1:1 as x increases. All reflections in ϕ-scan curves widen with x, indicating a decrease in the coherent X-ray scattering regions along the diffraction direction. This fact is in a good agreement with the decrease in the dimensions of the flat terraces in the basal plane, visible by atomic force microscopy. In
addition to $60^\circ$ twins, the $30^\circ$ rotational domains also appear with the increase of Sr concentration to 25.8%.

![Intensity vs. phi](image)

**FIG. 6:** \( \varphi \) scan about of the [00.1] axis on (1 0.10) reflection for films with different \( x \) (0%, 1.8%, 14%, and 25.8% from bottom to top). Amount of $60^\circ$ twins increases with \( x \). For \( x = 25.8\% \), 30 degree twins emerge.

**Transport measurements**

Transport properties also show up systematic dependencies on \( x \). The resistance per square (\( \rho \)) vs temperature for the representative films is shown in Fig. 7. All films have metallic type resistivity (\( \frac{\partial \rho}{\partial T} \)) in wide range of temperatures. The value of the resistivity per square tends to enhance progressively with Sr doping level for all the temperatures. This fact indicates that Sr atoms act as additional scattering centers and influence the mobility in such a way that the product of carrier mobility and concentration decreases with \( x \). The residual-resistance ratios (RRR), defined as ratios between the resistance at 300 K and minimal resistance at low \( T \), are summarized in Table I. RRR is about \( \sim 1.5 \). As obtained from the \( \frac{\partial \rho}{\partial B} \) slope all films are n-type. In Fig. 8 and Fig. 9 the boxes show carrier density and mobility as a functions of \( x \), respectively. Adding Sr increases the Hall density in the system and decreases the carrier mobility dramatically. It means that the Sr atoms acts as donors and scattering centers.

![Resistivity vs. temperature](image)

**FIG. 7:** The resistivity vs. temperature for four representative Sr doped Bi\(_2\)Se\(_3\) films (x=0.3%, 1.8%, 10.5%, and 15.7% from bottom to top). All \( \rho(T) \) dependencies exhibit metallic behavior with RRR\(~ 1.5\).

![Hall carrier density as a function of doping level](image)

**FIG. 8:** Hall carrier density as a function of doping level for 25 nm thick films (black squares). Red triangles correspond to Sr\(_x\)Bi\(_2\)Se\(_3\) crystals.

**Quantum transport**

For low temperatures, a pronounced \( B = 0 \) dip in magneto-resistance was observed for all studied films. Similarly to previous studies on thin films of Bi-chalchogonies, we attribute it to weak antilocalization. We fitted magneto-conductivity with Hikami-Larkin-Nagaoka (HLN) formula:

\[
\sigma(B) - \sigma(0) = -\frac{\alpha e^2}{2\pi^2 \hbar} \psi(\frac{1}{2} + \frac{\hbar}{4eB L_\varphi}) - \ln\left(\frac{\hbar}{4eB L_\varphi}\right)
\]

Here, \( \alpha \) is an adjustable prefactor; \( e, \hbar \) stay for electron charge and Plank constant, respectively; \( L_\varphi \) is adjustable phase coherence length, \( \psi \) is the digamma function.
Sr impurities do not affect the quantum transport.

**COMPARISON OF EPITAXIAL FILMS AND BULK SUPERCONDUCTING SINGLE CRYSTALS**

Absence of superconductivity in thin films motivated us to perform a detailed comparison with SC single crystals. The latter are remarkable by saturation of Sr real content around 6%, that is nearly independent of nominal composition $x$, for $x$ above 10%\(^\text{[12]}\). For all SC single crystals typical Hall density of $2 \times 10^{19}$ cm\(^{-3}\) and the critical temperature $T = 2.4-3$ K are highly reproducible in a number of different labs\(^\text{[12, 13, 24]}\). Sr-doped Bi\(_2\)Se\(_3\) always remains n-type\(^\text{[13, 15, 24]}\), despite the fact that divalent Sr replacing trivalent Bi should act as a strong acceptor. These strange issue is related to a rather complex tetradymite lattice structure. Dopants may be distributed over a large number of electrically inequivalent incorporation sites within unit cell consisting from three QLs separated by vdW gaps.

In the thin films we can tune both composition and Hall density beyond $x = 6\%$ and $n = 2 \times 10^{19}$ cm\(^{-3}\), respectively. Yet, we do not observe superconductivity.

Free carrier concentration of $n \approx 2 \times 10^{19}$ cm\(^{-3}\) is achieved already at $x = 2\%$, in both, thin films as well as bulk crystals. However, at higher Sr content in bulk crystals $n$ is stable with $x$, while it reaches $n \approx 7 \times 10^{19}$ cm\(^{-3}\) in thin films and saturates at that level for $x$ above 12\% (compare boxes and triangles in Fig. 8). These results suggest various mechanisms of doping in crystals and thin films.

It is not surprising therefore that mobilities (see Fig. 9) also display different behavior. In thin films mobility dramatically drops, while in the same range of $x$ between 1\% and 6\% scattering of carriers in bulk crystals is nearly composition insensitive.

Interestingly, much more pronounced distinction show up a crystal structure (see Fig. 4): as $x$ increases, $c$-lattice parameter in epitaxial films grows an order of magnitude faster than in bulk crystals (see triangles versus boxes in Fig. 4). This is a direct indication that Sr takes different positions in the lattice of the films and bulk crystals.

Another essential difference between SC crystals and thin films is the domain structure. Indeed, while the crystals consist of slightly misaligned, hundreds-of-microns sized blocks\(^\text{[13, 16]}\), Sr-doped films are composed of submicron-sized triangular twin domains with two opposite orientations. These domains are evidenced by the AFM pictures in Fig. 5 and XRD Phi-scans (Fig. 6). Unless special care is taken\(^\text{[26, 27]}\), even binary undoped Bi\(_2\)Se\(_3\) films on lattice matched InP substrates are heavily twinned. In our case, concentration of twin domains tends to increase with Sr content. Twinning means that the anti-phase domain boundaries interpenetrate the

**FIG. 9:** Hall carrier mobility as a function of doping level for 25 nm thick films (black squares). Red triangles correspond to Sr\(_x\)Bi\(_2\)Se\(_3\) crystals.

**FIG. 10:** The insert shows the weak antilocalization magnetoconductance at different temperatures (symbols) for $x = 10.5\%$ film (746) and their fits with HLN formula. Main panel shows the fitting parameter $\alpha$ (left axis) and phase breaking time $\ell_\phi$ as a function of temperature. The dashed line is $\propto T^{-0.5}$ fit.

The other Sr-doped films demonstrate similar values of $\alpha$ and $\ell_\phi(T)$ dependencies. This observations are consistent with numerous reports on non-doped films of Bi chalcogenides\(^\text{[18, 22, 23]}\). Thus, our studies indicate that
whole body of the film, thus promoting orders of magnitude faster diffusion of foreign atoms and governing redistribution of Sr atoms in the lattice. It is important therefore to understand whether domain boundaries and elevated c-lattice constant (Sr content and placement) in thin films are interrelated. Observation of novel properties (and superconductivity in the optimistic scenario) for single-domain Sr-doped films would be crucial experiment, that clarifies the role of grain boundaries. The growth of single-domain Sr-doped Bi$_2$Se$_3$ films however calls for sophisticated substrate interface engineering and has not been performed so far.

**DISCUSSION**

Apparently, the growth conditions in MBE and Bridge-man method are absolutely different: thin films are epitaxially assembled in vacuum at ≈570 K, with an excess flux of Se. This extra flux is unavoidable, and it is aimed to maintain stoichiometry of the growing Bi$_2$Se$_3$ film even in the presence of additional flux of Sr atoms. Growth of the bulk crystals starts by melting of encapsulated constituent elements Sr:Bi:Se with a molar ratio x:2:3 at a temperature 1120 K and ends at 900 K. So, the system stoichiometry is shifted towards the metal excess, and temperature is twice as large as for thin films. These two factors may provide much more probability for Sr dopant atoms to attain the most energetically favorable positions in the lattice. For thin films, at temperatures above 570 K thermal etching already starts to destroy the layer, making higher temperatures impossible. So, the dopant adatoms at the growing surface meet excess Se and may have not enough energy to occupy a "proper" superconducting-relative sites.

We may assume, that in bulk crystals Sr atoms are predominantly intercalated in vdW gap, while in thin films dopant atoms reside also on Bi sites and occupy different interstitial coordination positions inside quintuple layers. So, unlike bulk crystals, Sr atoms in the epitaxial layers may predominantly substitute Bi atoms and sit between the Bi and Se atomic sheets. In this case dopant atoms form different electrically active defects: Sr$_{Bi-1}$ along with Sr$i+1$. First, that simple model may well explain huge (above 1%) c-lattice parameter increase in epitaxial thin films with x ≈ 12%. And next, dual donor-acceptor nature of Sr impurity might also be responsible for observed unusual strong n-type doping (Fig.5) in Bi$_2$Se$_3$ films.

It was suggested initially that superconductivity in bulk Sr-doped Bi$_2$Se$_3$ crystals is achieved through intercalation. In other words, observed slight increase in the c-axis constant [13, 24] implies that Sr dwells in the Van-der Waals gap. Later, from STS experiments [28] two possible locations for Sr were derived: either intercalated in vdW gap or placed inside quintuple layer. Recently authors in [23] concluded that n-type Sr dopants are responsible for superconductivity and Sr atom position should be energetically metastable. Moreover, from atom-by-atom elemental analysis based on EDX mapping it was concluded, that in addition to substitution defect Sr$_{Bi-1}$ dopant atoms may form Sr$i+1$ various interstitial defects. Microstructural TEM investigations of Sr-doped Bi$_2$Se$_3$ thin films [17] revealed, that distance between Bi atomic sheets inside QL was compressed, while separation between the closest Bi planes in adjacent quintuple layers was expanded. In doped bulk samples an opposite behaviour for Bi-Bi inter and intra QL spacing was observed. All those results are direct and strong support for suggested structural explanation of qualitative distinction between non-superconducting thin films and superconducting bulk samples found in our work.

It is not necessarily that Sr atoms are randomly distributed in the lattice. We can't exclude formation of metal-riched nanoclusters [29, 30], flat inclusions [31], segregation [?], or even well arranged blocks [32]. However, in XRD similar imperfections are usually manifested just as a broadening of the reflections, while detection of the specific Sr-enriched structures by means of TEM is rather challenging. To the best of our knowledge none of the published TEM pictures of SC Sr$_2$Bi$_2$Se$_3$ demonstrate explicitly locations of Sr atoms. Small atomic number of Sr and low concentration ( 1.2 at. %) even in SC bulk crystals, along with probable stochastic distribution make TEM imaging of Sr a rather complicated task. Yet eventually, actual dopant housing is a key for understanding their impact on carrier concentration and superconductivity.

**CONCLUSION**

In our paper we have grown a series of Sr-doped Bi$_2$Se$_3$ films on (111) BaF$_2$ substrate with various Sr content and thickness. These films are not superconductive and differ strongly from bulk crystals by structure, morphology and transport properties. We explain these differences by various positions, that Sr atoms take in the crystalline lattices: mostly intercalation in crystals and predominantly substitution/interstitial in thin films. These differences are due to different growth temperature (~1100 K for crystals and ~550 K for films), distinct liquid-solid and vapour-solid crystal formation mechanism, unequally maintained stoichiometry, and domain structure of the films. We believe that the path to superconductivity in epitaxial Sr-doped Bi$_2$Se$_3$ films comes through the adjustment of the Sr-atoms subsystem by co-doping and/or interface engineering to attain a proper Sr atom distribution. Another possibility to achieve superconducting doping structure is to fine tune film stoichiometry through lowering Se to BiSe flux ratio while using a compound bismuth-selenide effusion source.
Therefore, a lacking so far understanding (both theoretical and experimental) where the Sr atoms should and use to sit, is highly demanded.

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