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Reflections on the First Year of PLD of High Temperature Superconducting Thin Films and Some Recent Advances in PLD of Topological Superconducting NbN-Bi_2Se_3-Au Junctions

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Abstract: Some historical reminiscences are described concerning the first year of the development and optimization of the pulsed laser deposition (PLD) technique for the deposition of high quality cuprate thin films of the high temperature superconductors (HTS). Recently, we have been involved in the search for Majorana fermions (MFs) in topological superconducting thin films. Superconductivity is induced in the doped topological insulator Bi_2Se_3 by the proximity effect when in contact with an s-wave superconductor such as NbN. Junctions of NbN-Bi_2Se_3-Au were prepared by PLD of the corresponding thin films. Conductance spectra of these junctions showed robust zero bias conductance peaks (ZBCPs) and coherence peaks. The ZBCPs are attributed to same-spin triplet superconductivity in the Bi_2Se_3 layer at the interface, which apparently masks any presence of the MFs.

Key words: Laser ablation deposition, thin films, multilayers, junctions, superconductivity, topological insulators.

1. Introduction

The present paper is a written version of an invited talk I gave in ICMAT 2013, the 7th International Conference on Materials for Advanced Technologies, on July 3 2013, in Singapore. This talk was delivered in a symposia dedicated for the celebration of the 25th anniversary of the application and optimization of the pulsed laser deposition (PLD) technique for thin films deposition of the cuprate high temperature superconductors (HTS). As such, this paper comprises of two parts. The first one describes how the pulsed laser deposition process of HTS thin films was developed and optimized during the first year following the discovery of these materials. The second part is a study of the epitaxial growth and surface morphology of thin topological films of Bi_2Se_3, as well as conductance spectroscopy measurements of junctions made of these films in contact with the conventional s-wave superconductor NbN, all prepared by the PLD technique. While the first part is a kind of the historical, the second part is a state of the art research of proximity induced topological superconductivity, which might be useful in future quantum computers.

1.1 Reminiscences on the History of PLD of the HTS Thin Film

Right after the discovery of the high temperature superconductors in 1986, it was clear that high quality thin films of these materials are highly needed. Efforts to produce these films by standard sputtering or evaporation techniques faced problems of losing stoichiometry, and therefore the loss of quality or

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superconductivity altogether. Pulsed laser deposition, which was previously used for the deposition of binary semiconductor compounds, seemed promising for keeping the stoichiometry of the HTS materials in the films. Nevertheless, it took about a year to optimize parameters and fabricate *in-situ* HTS films by the PLD technique. Working in the field of pulsed laser ablation prior to these efforts, mostly for the purpose of etching of polymers, semiconductors and insulators, I quickly shifted to deposition of thin films by PLD. Actually, our efforts in PLD were conducted in parallel to those of Venky's group in Bellcore, but they had preceded us in submitting their results for publication by about half a year [1, 2].

It turned out that optimization of the deposition parameters in 1987-1988 took longer than expected, mostly due to the incomplete understanding of the oxygen role in the stability and crystallization of the HTS thin films. Since the 1-2-3 HTS compound $YBa_2Cu_3O_{7-\delta}$ (YBCO) had a T_c above that of liquid nitrogen, most groups worked on it first. It was believed that the PLD films always copied the stoichiometry of the target, but this is of course true only for stable phases, which luckily the 1-2-3 YBCO, happened to be. At some point, we were amazed to find that even when starting with a 2-1-1 target (the "green phase" of YBCO, Y_2BaCuO_5 which is insulating), the resulting films were mostly of the 1-2-3 phase, with some extra impurity phases. But the most problematic issue was the oxygen effect on the stability of the films. Using vacuum deposition, many researchers failed to obtain good YBCO films. The problem was that chemically, below about 5-10 mTorr oxygen pressure, hot YBCO is unstable and decomposes by losing Cu_2O which is quite volatile. Actually, at the beginning we did not realise this, and just by trial and error found that oxygen pressure of about 100 mTorr is needed during the deposition process in order to obtain high quality thin films by PLD. Only about a year later, when I was on Sabbatical at the IBM Research Center in Yorktown Heights, Helen Raffy, a chemist, explained this issue to me. Another important parameter was the deposition temperature which had to be around 700-800 °C, and that posed problems with the heater blocks that had to work close to their limit. Gluing of the wafers to the heater block with silver paste, decrease the thermal gradient between the two, and relaxed a bit the demands on the heaters. Some people still use this gluing technique even today. Oxygen annealing after deposition was also an issue. It was known from the annealing of ceramics samples that most of the oxygen intake for optimally doped YBCO (the T_c = 90 K phase) occurs at around 400 °C in ~1 atm Oxygen pressure. So we followed this procedure *in-situ* after the deposition process and obtained the first high quality *in-situ* YBCO films [2]. Other groups however, used an additional *ex-situ* annealing step at that time [1].

In the IBM Research lab at the time (1989), a large group of about 30 researchers was working on the HTS materials. There was a weekly seminar of this group where people presented "work in progress" results. We had visitors from all over the world almost every week, and all this contributed to the advancement of the HTS research. One day, we had a distinguished visitor from Bellcore, Venky Venkatesan. He told us that he was delighted to see our APL paper from 1988 [2], reporting on thin YBCO films prepared by PLD, since he got a bit nervous getting messages from people of other labs who complained to him that they could not reproduce his results and obtain good YBCO films by PLD. Well, that was apparently due to the low oxygen pressure used during the deposition process at the time [1]. So far for nostalgia, and now we shall continue with some recent work of our group on topological insulators and topological superconductors.

1.2 Background: Proximity Induced Topological Superconductivity

In the last couple of years, we had been involved in

the search for Majorana fermions (MFs) in topological superconducting (TSC) thin films [3, 4]. The idea was to induce superconductivity in the doped topological insulator Bi_2Se_3 by an s-wave superconductor via the proximity effect. For this we prepared NbN-Bi_2Se_3-Au junctions by PLD and measured their conductance spectra. The results showed robust zero bias conductance peaks (ZBCP), which indicated unconventional superconductivity, but did not provide a conclusive evidence for the presence of MFs. In the following, some of these results and Se loss problems in the Bi_2Se_3 films will be discussed.

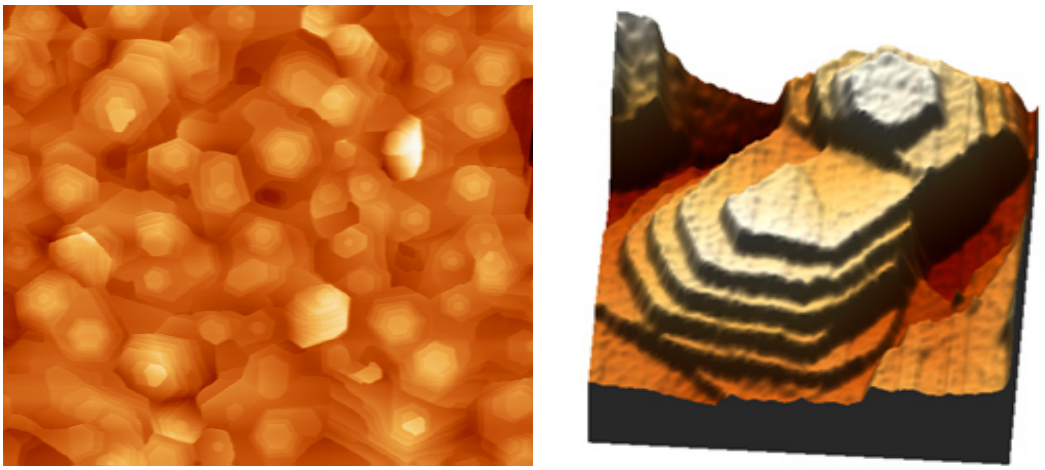
2. Experiments: Thin Films and Junctions Prepared by PLD

Deposition of the Bi_2Se_3 films by the 355 nm laser pulses was done under vacuum and temperatures of the heater block in the range of 250-400 °C, where the wafer was clamped to the block. The actual deposition temperatures were therefore lower, about 200-300 °C. The films structure was checked by using X-ray diffraction and their surface morphology by atomic force microscopy (AFM). At laser fluences of about 1 J/cm^2, Bi rich films were obtained and only when the laser fluence was reduced to about 0.4 J/cm^2 that the desired Bi_2Se_3 phase was achieved. The lower fluence on the target was needed in order to have less energetic Se atoms and ions in the laser ablated plume, which enhanced their sticking to the film and prevented higher Se losses. The morphology of a film deposited on a (111) wafer of $SrTiO_3$ is shown by the AFM images of Fig. 1. These images show that the film grew epitaxially with an ordered in-plane hexagonal structure. X-ray diffraction of these films showed the correct hexagonal structure with the *c-axis* (c = 2.84 nm) normal to the wafer.

The NbN films were deposited at 600 °C heater block temperature and under 40 mTorr of N_2 flow. A high laser fluence of about 7 J/cm^2 was used on a Nb metal target at a laser repetition rate of 10 Hz to avoid oxidation of the Nb in the plume. When the base pressure was in the low 10^{-7} Torrs, the NbN films had a T_c of about 12 K. The gold films were deposited by PLD under vacuum at 150 °C, also with a high laser fluence of about 5 J/cm^2 on the gold target. The NbN-Bi_2Se_3-Au junctions were prepared by either the use of a shadow mask for overlap junctions, or by a multi-step photolithographic process with Ar ion milling for the ramp junctions. As a tunneling barrier we used the thin native oxide of NbN (1-2 nm) which is formed within an hour when the NbN films are exposed to ambient air [4, 5].

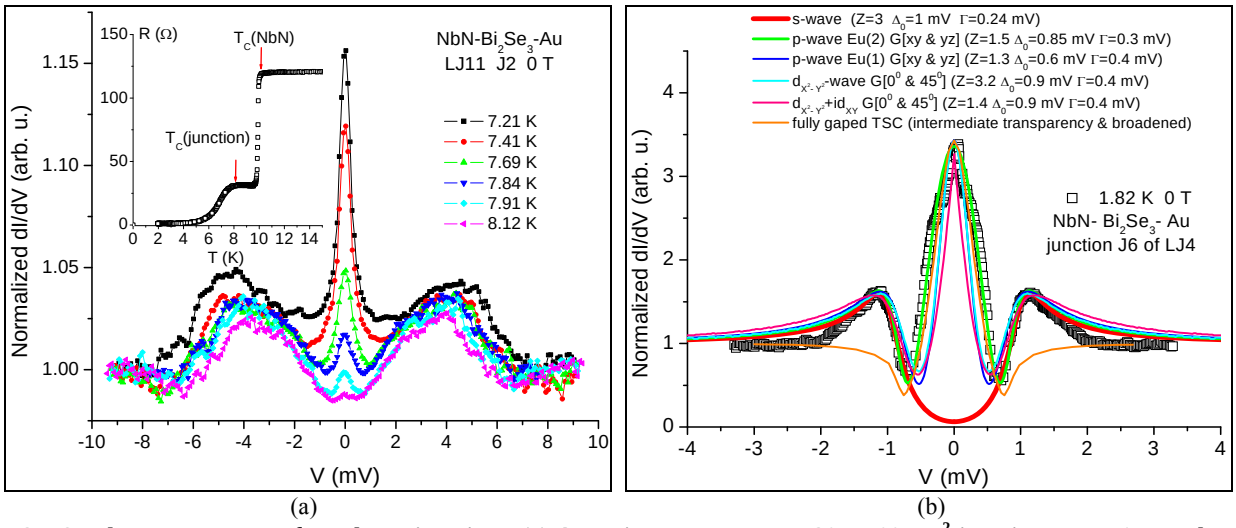
3. Results and Discussion: Conductance Spectra

Fig. 2 shows conductance spectra of two large



(a) (b)

Fig. 1 (a) A 2 × 2 μm^2 2D AFM image of a laser ablated Bi_2Se_3 film on (111) $SrTiO_3$. (b) a 0.3 × 0.3 μm^2 3D zoom-in on a top part of the left panel.

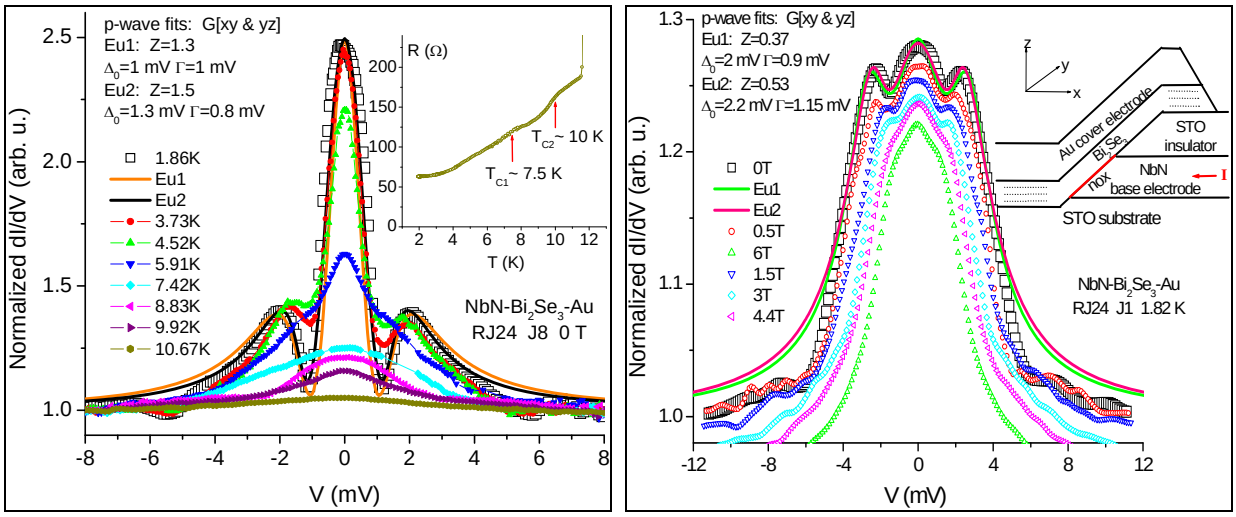


(a) (b)

Fig. 2 Conductance spectra of two large junctions, (a) At various temperature, 30 × 100 μm^2 junction area, 70 nm NbN-20 nm Bi_2Se_3-70 nm Au together with the resistance versus temperature in the inset. (b) 150 × 100 μm^2 junction area, 70 nm NbN-100 nm Bi_2Se_3-100 nm Au together with various BTK fits.

overlap junctions (the data of Fig. 2b here is that of Fig. 5d of Ref. [4]). Fig. 2a shows that the ZBCP of the main panel decays versus temperature and disappears at the proximity induced transition temperature of the junction T_c(junction) as seen in the inset. Above this temperature and up to the T_c(NbN) of the NbN electrode only the coherence peaks remain. The proximity effect in the Bi_2Se_3 is thus demonstrated. Fig. 2b shows that singlet s-wave pair potential (PP) could fit the coherence peaks of the conductance spectra but not the ZBCP, while a fully gapped TSC could barely fit the ZBCP and the two dips beside it, but not the coherence peaks. We therefore tried singlet d-wave PPs ignoring the hexagonal symmetry of Bi_2Se_3, but compensating for it by taking weighted tunneling contributions from the node and antinode directions while keeping the same fitting parameters Z, Δ_0 and Γ for both orientations. This weighted sum of the calculated individual conductance along the anti-node $G(0°)$ and node $G(45°)$ directions amounts to $a[G(0°) - 1] + b[G(45°) - 1] + 1$ where a and b are fit parameters. Fig. 2b shows that the fits improved, but not sufficiently to reproduce the whole width of the measured ZBCP. Finally, we tried the odd-parity triplet $p_x + ip_y$ PP which breaks time reversal symmetry. Following [6], we used $\Delta_{\uparrow\uparrow} = \Delta_0 \sin\theta(\cos\varphi + \sin\varphi)$ and $\Delta_{\uparrow\uparrow} = \Delta_0 \sin\theta(\cos\varphi + i\sin\varphi)$ PPs where θ and φ are the polar and azimuthal angles, for the corresponding Eu1 and Eu2 symmetries, while $\Delta_{\downarrow\downarrow} = \Delta_{\uparrow\downarrow} = \Delta_{\downarrow\uparrow} = 0$. As before, we sum over weighted contributions to the conductance from two different interfaces (xy and yz, where xy represents the a-b plane of the Bi_2Se_3 layers), and keep the same basic fitting parameters Z, Δ_0 and Γ for both interfaces. Fig. 2b shows that while the best fit using the Eu1 PP fails to fit the ZBCP, the Eu2 PP fits the data quite well. Next we show that such good fits are also obtained in much smaller ramp-type junctions where the combined contribution to the conductance from the xy and yz planes is evident (the inset of Fig. 3b).

Fig. 3 shows normalized conductance spectra obtained on ramp junctions whose cross section is shown schematically in the inset of Fig. 3b. At low temperatures and under zero magnetic field, Fig. 3a show tunneling-like spectra with robust ZBCP and coherence peaks similar to those of Fig. 2, while Fig. 3b shows Andreev-like spectra, but still with clear ZBCP and coherence peaks. The low temperature spectra of these figures could be fitted reasonably well using the triplet Eu1 and Eu2 PPs. Fig. 3a also shows spectra at different temperatures which reveal interesting



(a) (b)

Fig. 3 Conductance spectra of two 5 × 0.5 μm^2 area ramp junctions with 20 nm thick Bi_2Se_3 layer on the same wafer, together with p-wave BTK fits at low temperatures. (a) At various temperatures, with the resistance versus temperature in the inset, (b) under various magnetic fields normal to the wafer, with a schematic cross section of a typical ramp junction in the inset ("nox" in the inset stands for the native oxide).

correlation with the resistance versus temperature results of the inset to this figure where two kinks are found at T_{c1} ~ 7.5 K and T_{c2} ~ 10 K. The robust ZBCP of ~1 mV width persists up to about T_{c1}, while above it and up to T_{c2} only a broader ZBCP of ~2 mV width remains. This is apparently due to the merging of the decaying ZBCP and coherence peaks with increasing temperature, but could also result from different surface and bulk contributions at the chemical potential to the conductance (see the ARPES data for pure Bi_2Se_3 of Ref. [7]). Fig. 3b shows that with increasing magnetic field at low temperature the spectra become narrower, decay in height, and smeared as the ZBCP and coherence peaks merge with one another. The decreasing conductance at high bias and high fields in Fig. 3b is due to flux flow. In all our junctions we had never seen a ZBCP increasing with field as in recent studies on nano-wires [8, 9]. From the good fits of the data in Figs. 2b and 3, we conclude that also in small ramp junctions with different transparencies, the triplet $p_x + ip_y$ PP describes our results well.

Two odd parity triplet PPs allowed by symmetry in the Bi_2Se_3 hexagonal lattice, Δ_2 and Δ_4, were found by Fu and Berg [10]. Of these, Δ_2 supports MFs while Δ_4 does not. Since both PPs can coexist in a proximity induced TSC, it is possible that we observe Δ_4 which might originate in the bulk states at the Fermi level [7]. Δ_2 which originates in the surface states can still exist in our junctions, but is probably masked by the dominant Δ_4 contribution to the ZBCP. It is therefore essential to eliminate the bulk contribution (due to the Se loss in the films), and then the MFs might be observed.

4. Conclusions

We found a signature of proximity induced triplet superconductivity by NbN in the doped topological insulator Bi_2Se_3. Conductance spectra of various junctions with different transparencies that have robust ZBCPs and coherence peaks, could be fitted quite well using the chiral $p_x + ip_y$ pair potential. Thus, the observed ZBCPs of this odd parity, same-spin triplet pairs represent zero energy surface bound states which apparently do not originate in Majorana fermions.

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