

Joining Technique of Coated Conductors by Pastes Including Nano-sized Metal Particles

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METI

Ministry of Economy, Trade and Industry



This work has been supported by the Ministry of Economy, Trade and Industry (METI) and Japan Agency for Medical Research and Development (AMED) and New Energy and Industrial Technology Development Organization (NEDO).

Various applications of C.C.

We have concentrated to REBCO magnets.

Cables

Transformers

FCL

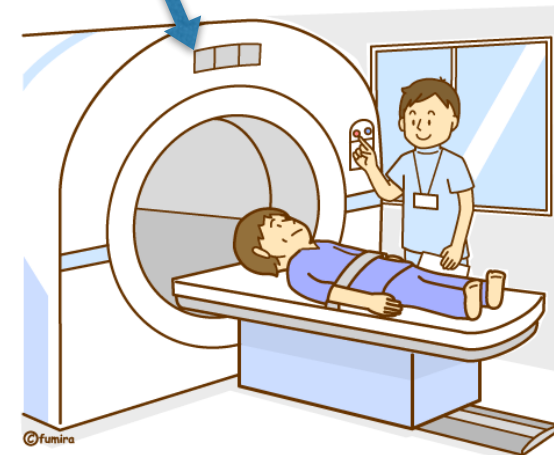
Motors

Generators

SMES



REBCO magnets



MRI magnet

Jointing is an indispensable technology in all application field of REBCO coated conductors (C.C.)

Comparison of previous techniques of jointing

Method	Resistance	Tensile strength	Jointing atmosphere	Jointing temperature	O ₂ -annealing
Solder joint [*1]	50 ~ 100 nΩ	800 N	Air	~ 220°C	Unnecessary
Diffusion joint of silver layer [*2]	6 ~ 10 nΩ	~ 1 kN	O ₂	300 ~ 400°C	~ 12 hours
Superconducting joint [*3]	0 Ω	Unknown	O ₂	800 ~ 850°C	post annealing / long slow cooling

*1: M. Sugano *et al.* “Stress tolerance and Fracture Mechanism of Solder Joint of YBCO Coated Conductors”, ASC 2006.

*2: J.Y. Kato, *et al.*, Physica C445-448(2006)686.

*3: Y. Park, *et al.*, NPG Asia Materials (2014) 6, e98. / see also T. Nagaishi *et al.*, ICMC and CSSJ 50th, 3A-p02(2016)

Demands for jointing technique

Handy & post-O₂ annealing-free

Low jointing resistance

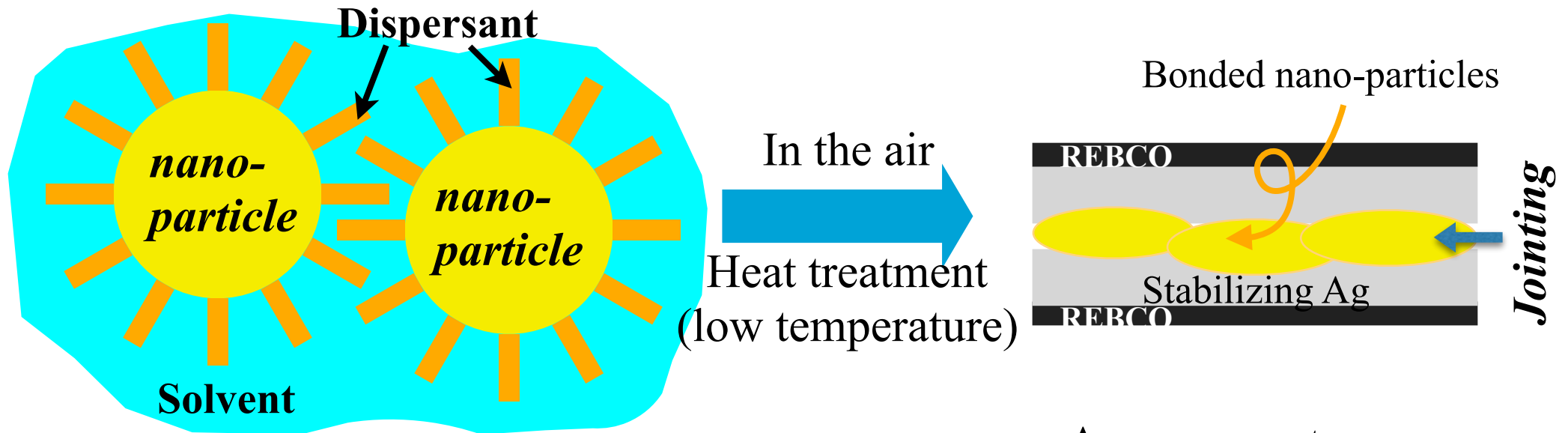
Tensile strength at the same level as solder jointing

Jointing technique that can be used at factories.

How to achieve the targets of this work

Our approach :

Gold (Au) nano-particle paste/ Silver (Ag) nano-particle paste



Nano-particle metal pastes

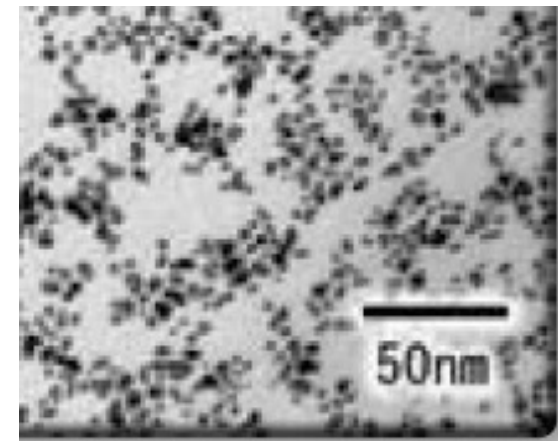
Joining by Au nano-pastes

AU NANOMETAL: ULVAC Inc.

Joining by Ag nano-pastes

L-Ag1 TeH: ULVAC Inc.

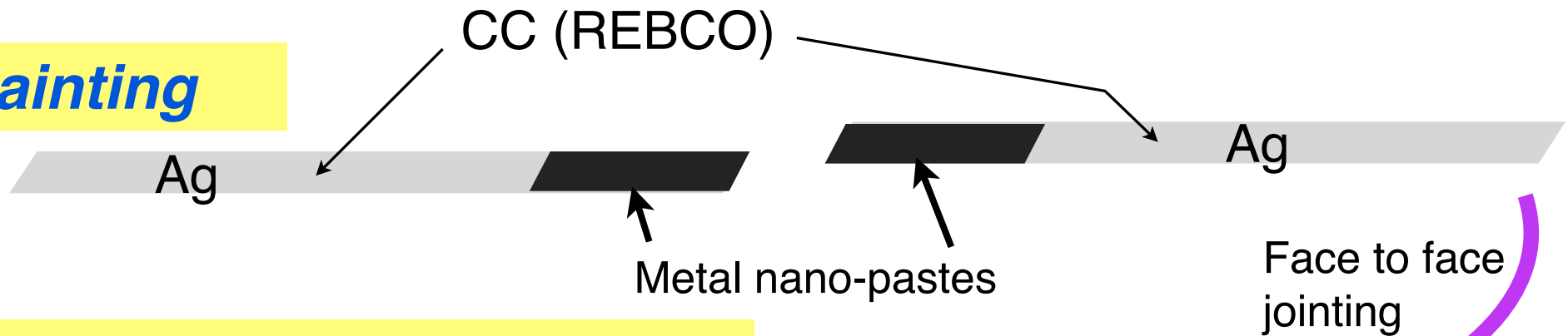
e.g. Au nano-paste



Particle-size ~ 5 nm

Experimental procedure:

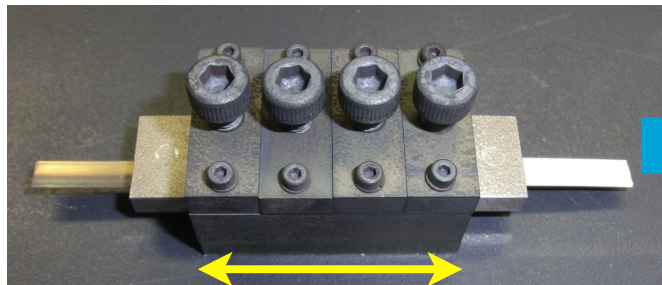
Painting



Face to face superposition

Heat treatment

Fixed by screw

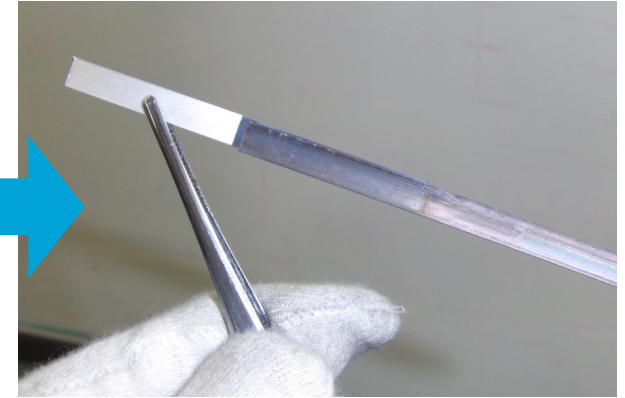


40 mm - 160 mm

Constant-temperature bath

Atmosphere : **Air**

100, 150, 200, 250°C
(0.5 - 2 hours)



Characterization

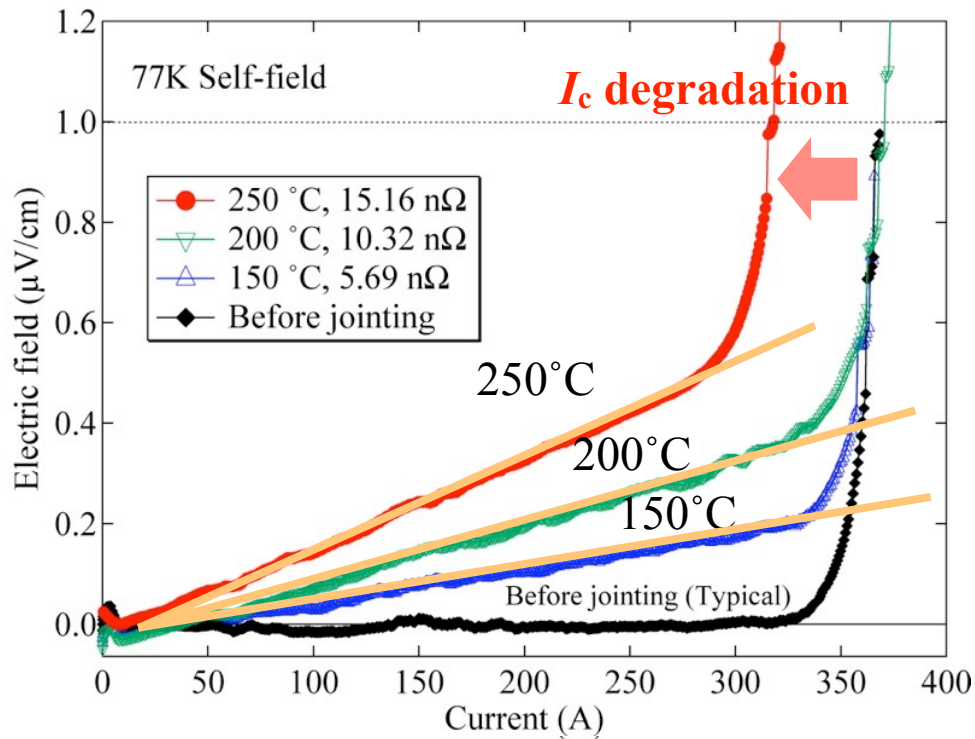
- I-V measurement
- Tensile destructive test
(Autograph, Shimadzu corp.)
- SEM observation

Results (*I*-*V* characteristics)

GdBCO c.c.

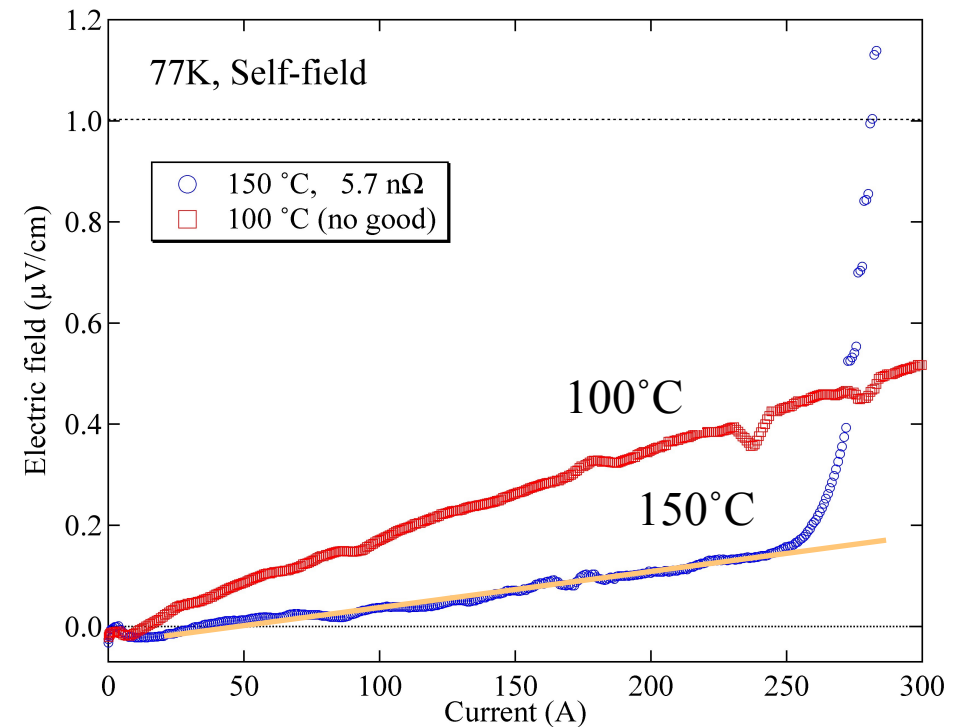
Au nano-paste jointing

Jointing area : 10 mm W, 80 mm L



Ag nano-paste jointing

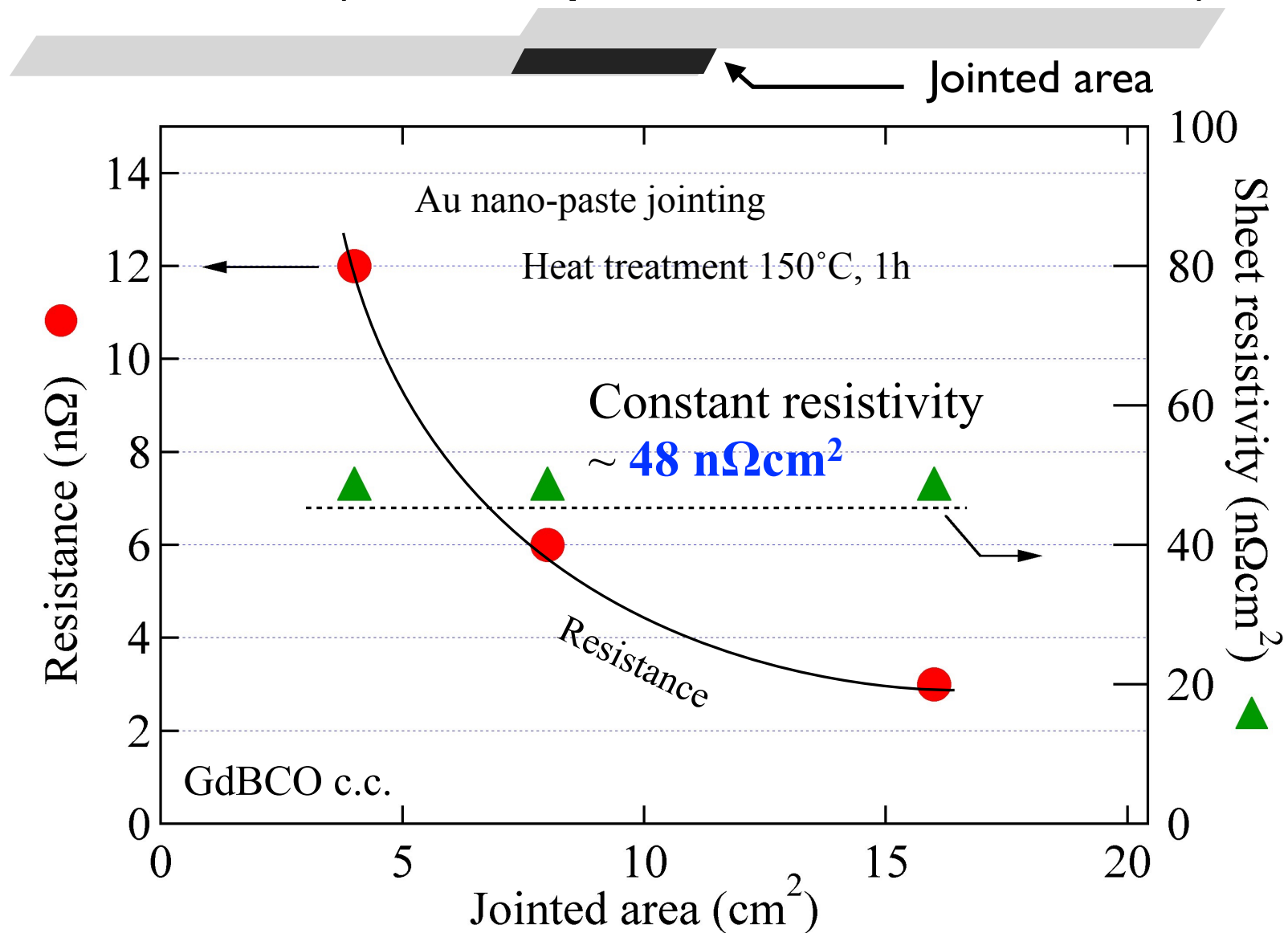
Jointing area : 10 mm W, 80 mm L



Jointed temperature	Resistance (nΩ)			<i>I_c</i> degradation
	100 °C	150 °C	200 °C	250 °C
Au nano-paste	no good	5.69	10.32	15.16
Ag nano-paste	no good	5.70	10.10	-

Suitable temperature range for jointing = 150 - 200 °C

Results (Area dependence of resistance)

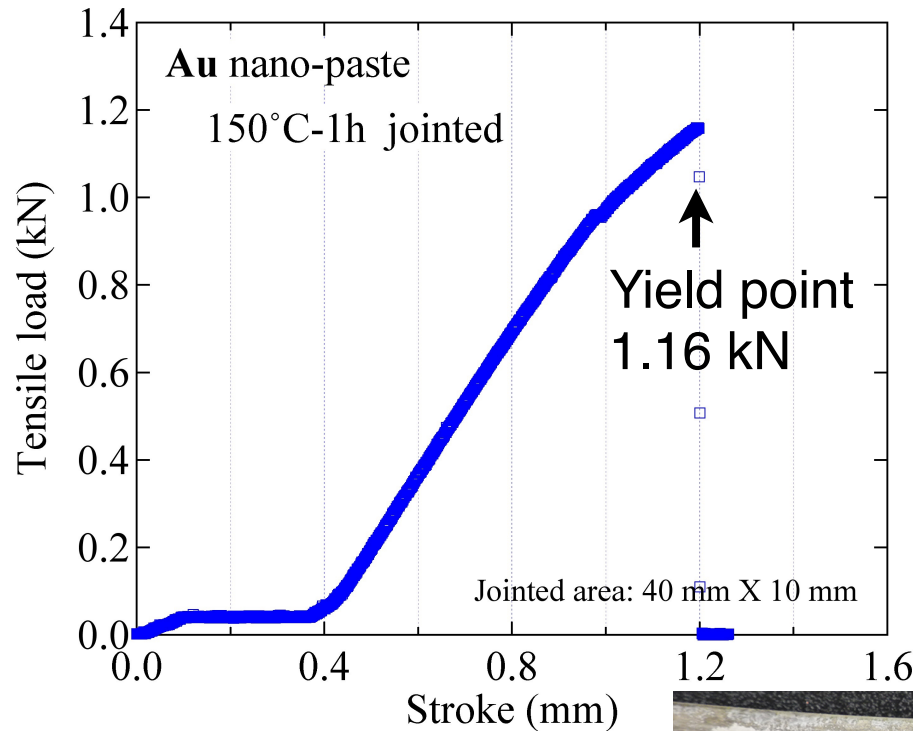


The constant sheet resistivity was maintained for different jointing areas.

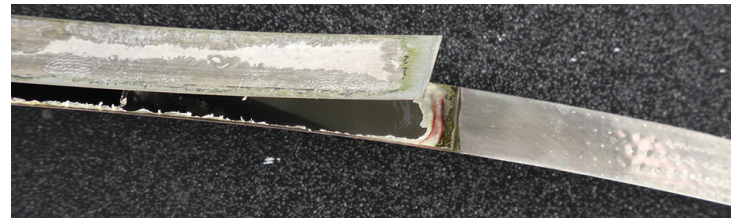
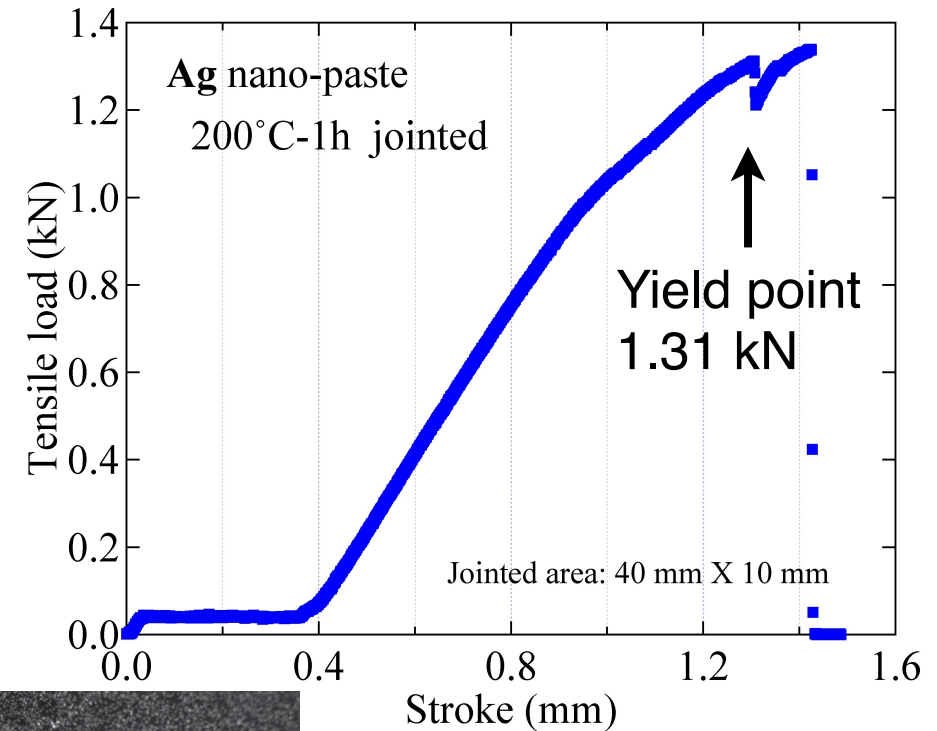
Results (Tensile strength)

GdBCO c.c.

Au nano-paste jointing



Ag nano-paste jointing



Peel off in a boundary of REBCO and silver.

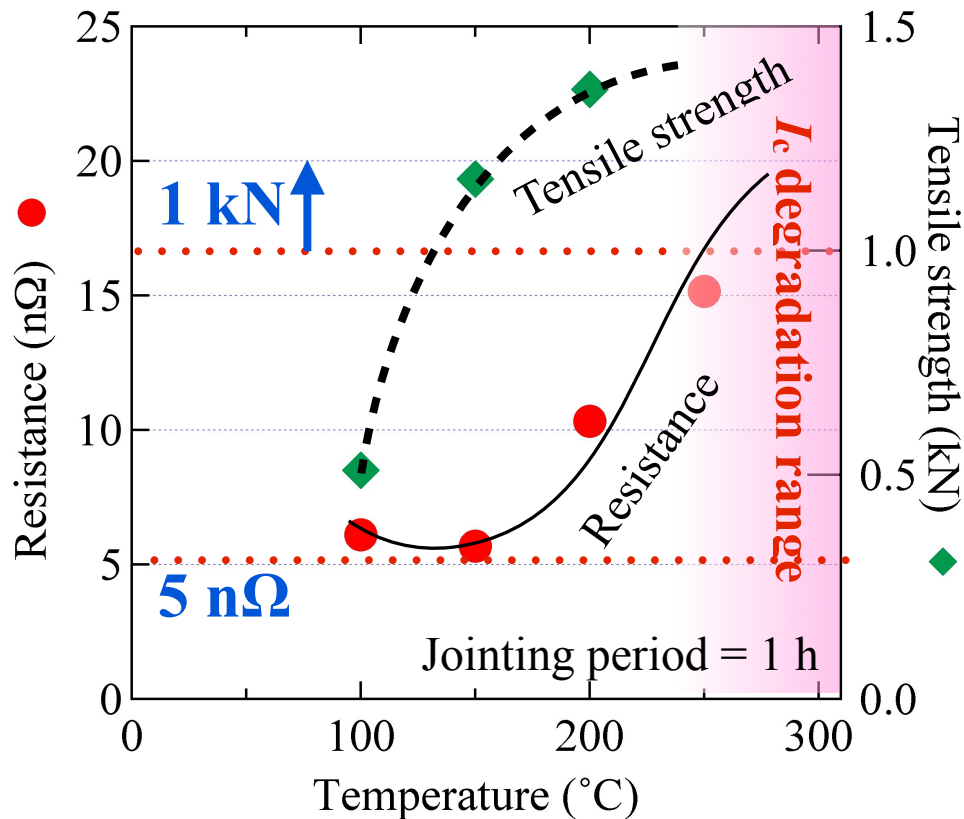
The tensile strength exceeded 1 kN.

It was stronger than solder jointing.

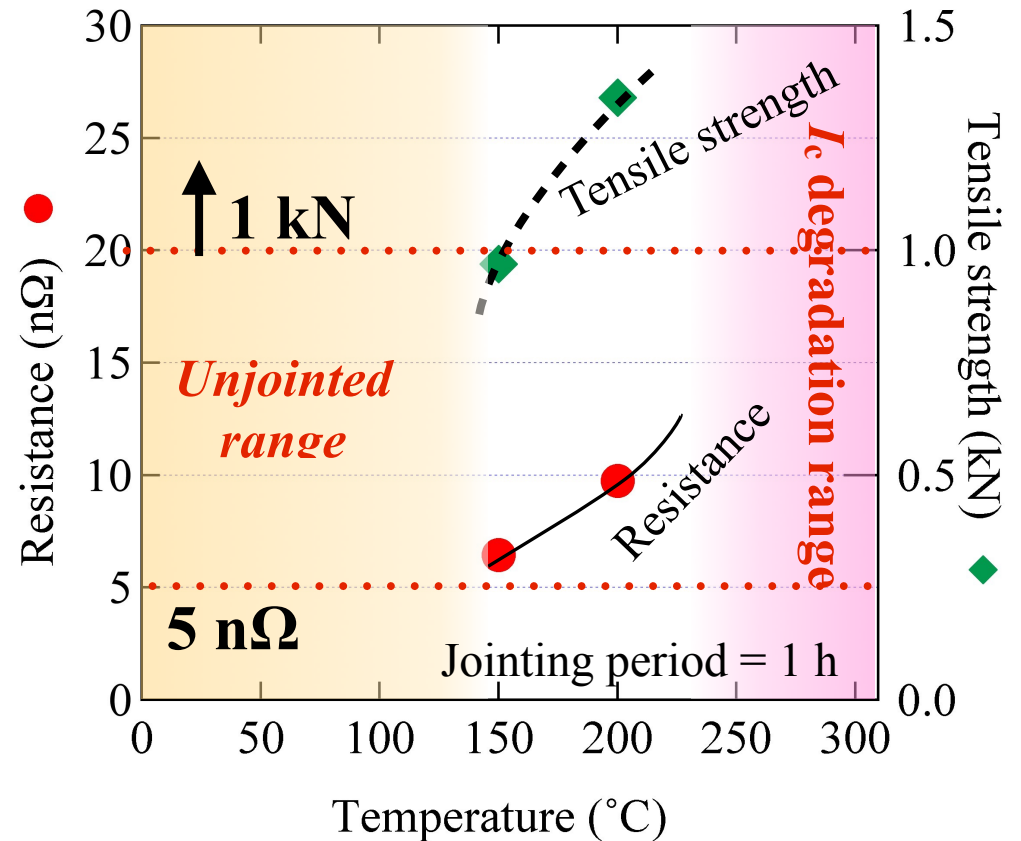
Results (Summary of Temperature dependence)

GdBCO c.c.

Au nano-paste jointing

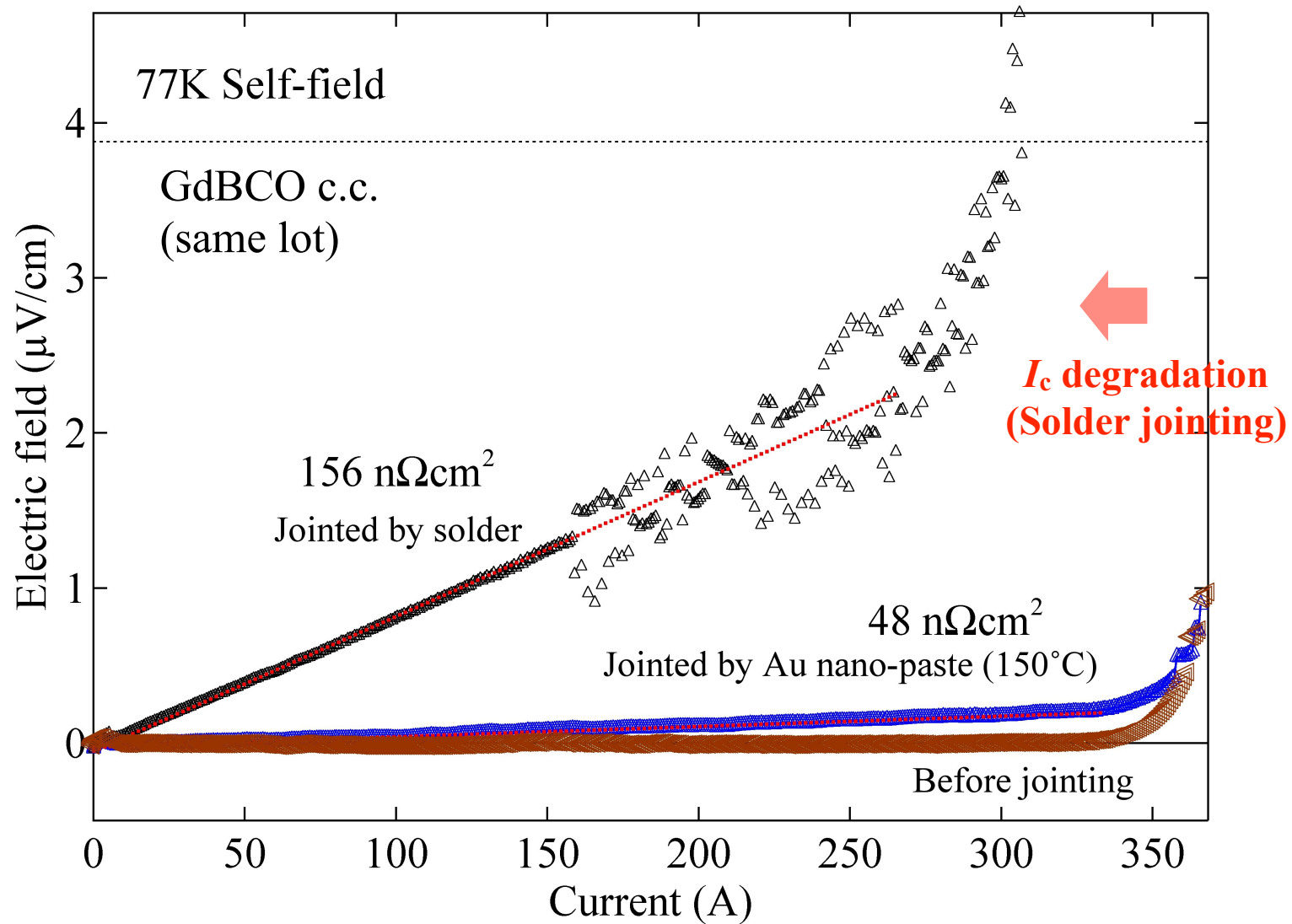


Ag nano-paste jointing



Suitable temperature for jointing ~ 150°C

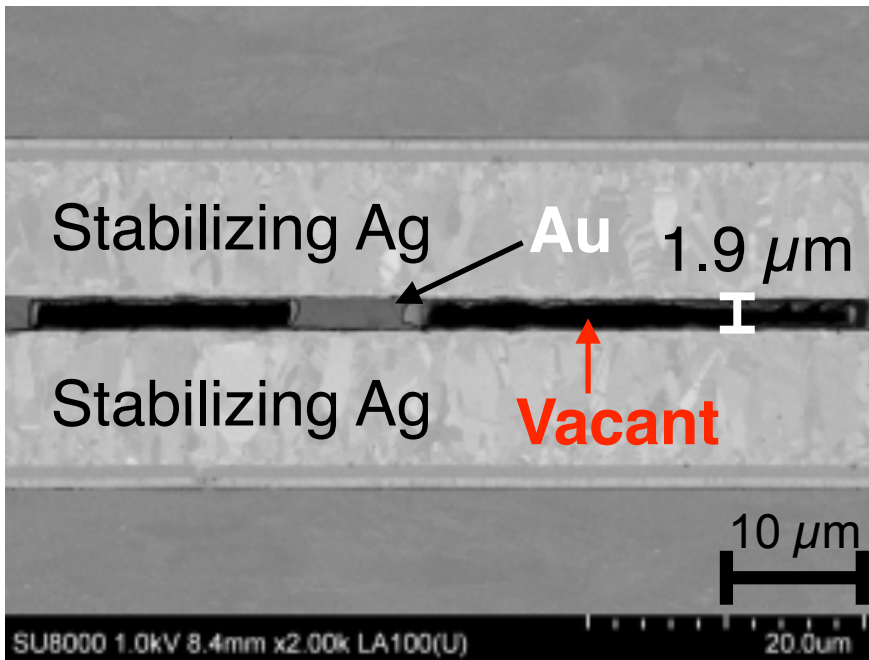
Results (Comparison with solder jointing)



Sheet resistivity of nano-paste was less than 1/3 of solder jointing.

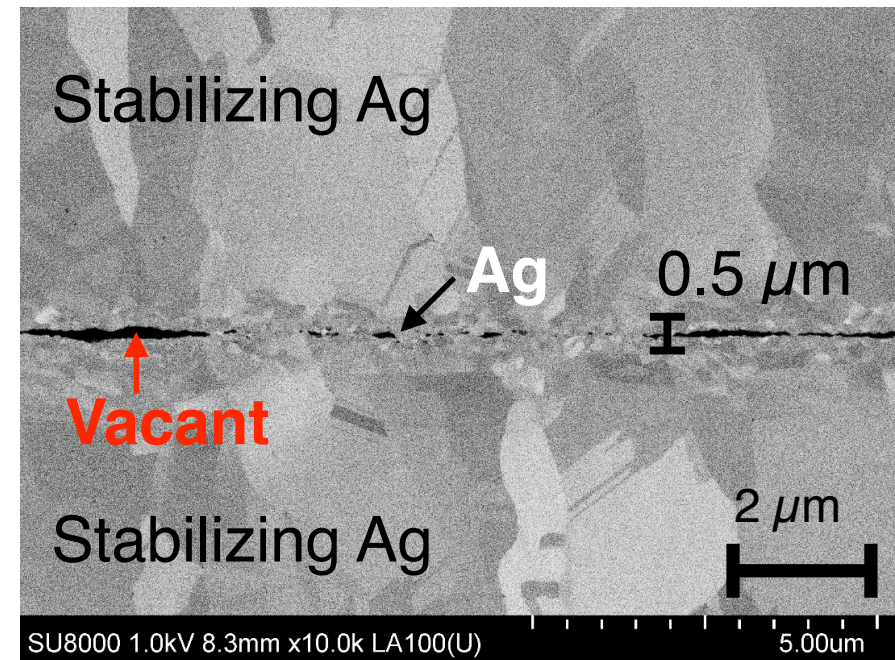
Cross sectional SEM observation

Au nano-paste jointing



T. Kato@JFCC

Ag nano-paste jointing



T. Kato@JFCC

*There were vacant space in jointed area.
—> Possibility of lower resistivity*

Short summary of nano-particle pastes jointing

Jointing by **Au nano-paste** and **Ag nano-paste**

Handy & post-O₂ annealing-free

Heat treatment temperature < **200°C** in **Air (1 hour)**

*(Suitable temperature of jointing was around **150 °C**)*



Unnecessary of post-O₂ annealing

Low jointing resistance

Sheet resistivity = **48 nΩcm²**

It is corresponds to **3 nΩ** (@1cmX16cm)

Tensile strength > 1 kN

It is stronger than solder jointing.

Next step

Toward lower resistivity of jointing

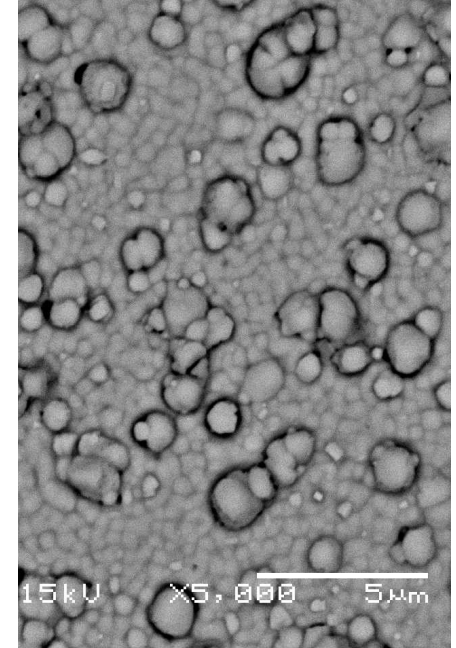
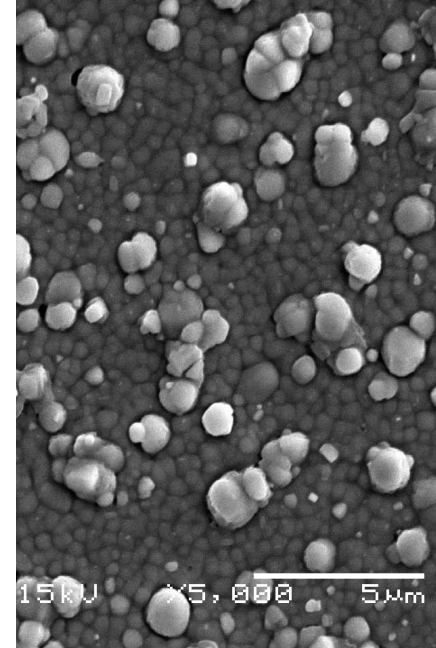
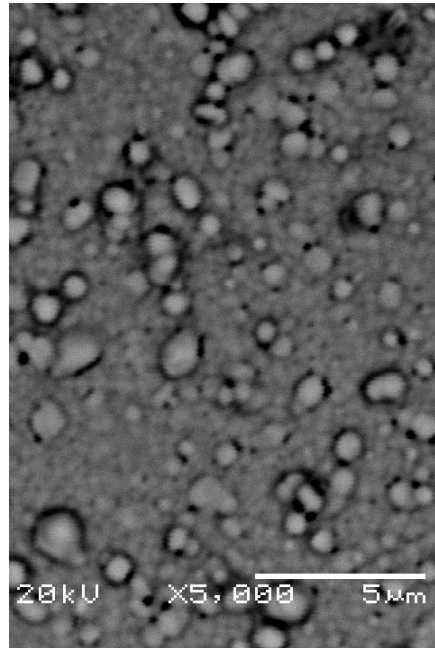
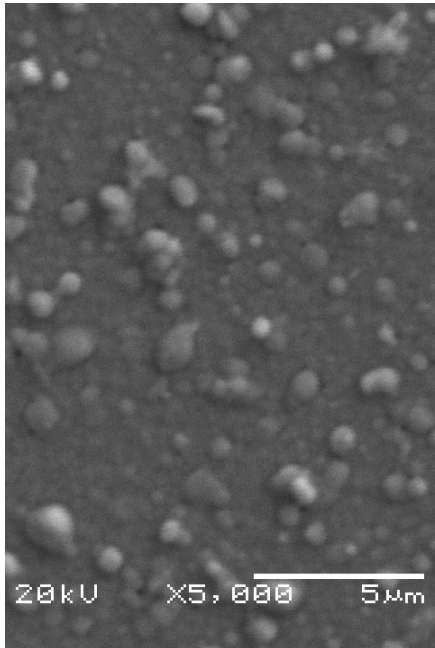
1. Decrease of vacant space

2. Influence of kind of REBCO materials etc.

Comparison between the different REBCO coated conductors

GdBCO
(thickness $\sim 1.2 \mu\text{m}$)

EuBCO
(thickness $\sim 1.2 \mu\text{m}$)



SEI

BEI

SEI

BEI

Similar morphologies of the REBCO surface



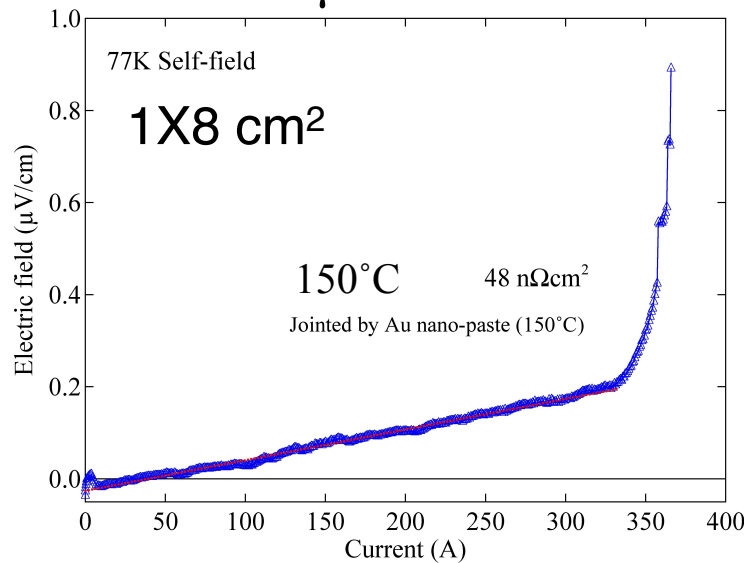
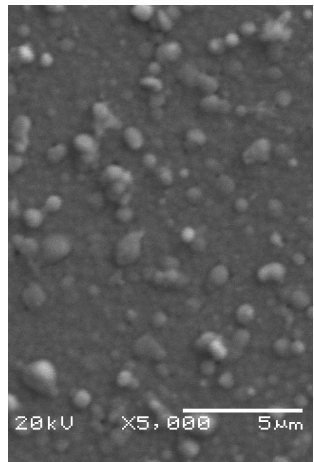
Jointing



Jointing

Influence of kind of REBCO

GdBCO
(thickness $\sim 1.2 \mu\text{m}$)



Jointed
@150°C

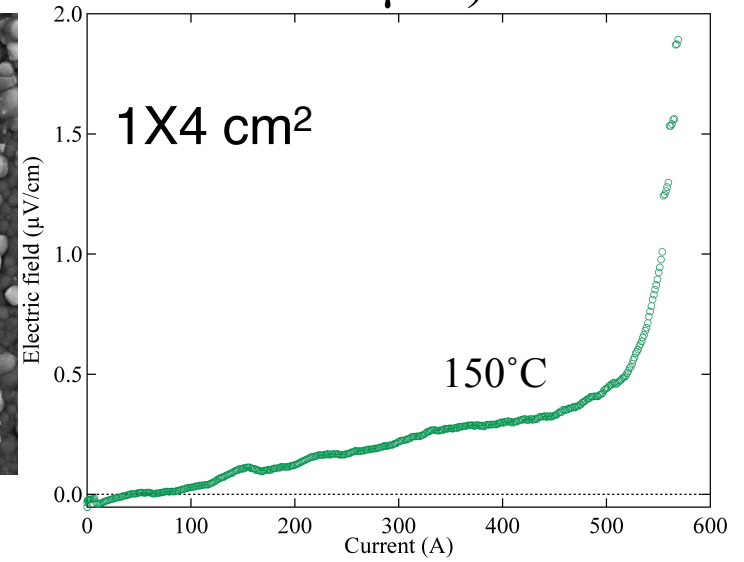
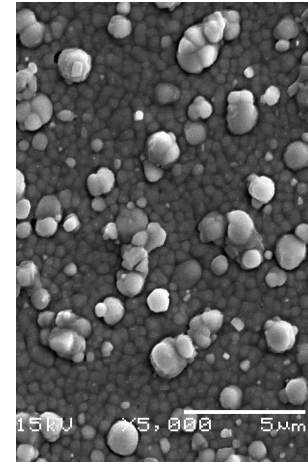
$$48 \text{ n}\Omega \cdot \text{cm}^2$$



$$R = 3.0 \text{ n}\Omega$$

10 mm W, 160 mm L

EuBCO
(thickness $\sim 1.2 \mu\text{m}$)



Jointed
@150°C

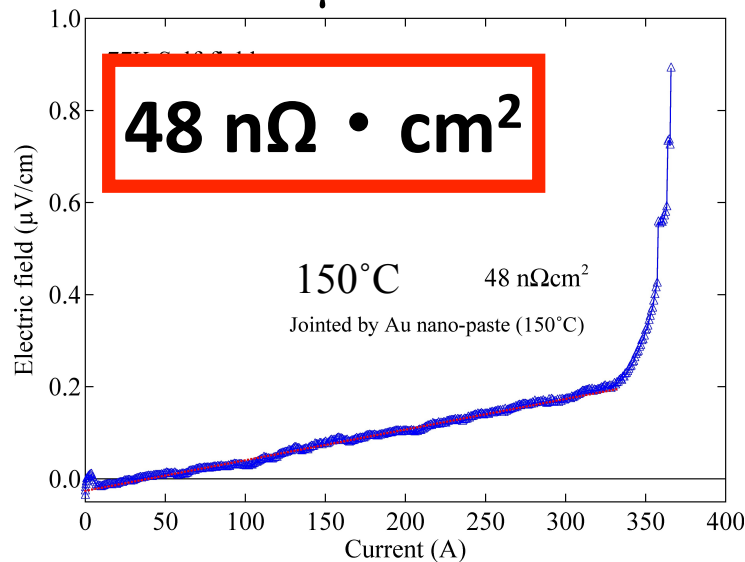
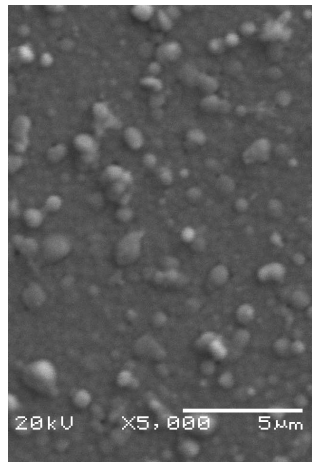
$$16 \text{ n}\Omega \cdot \text{cm}^2$$



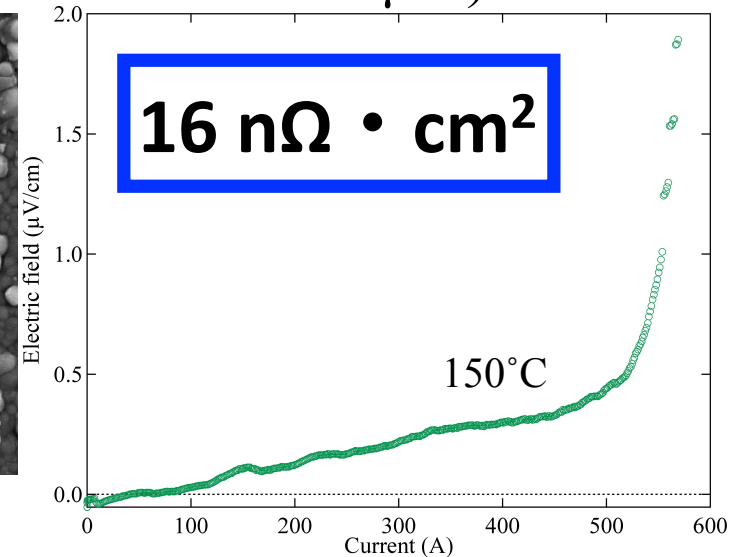
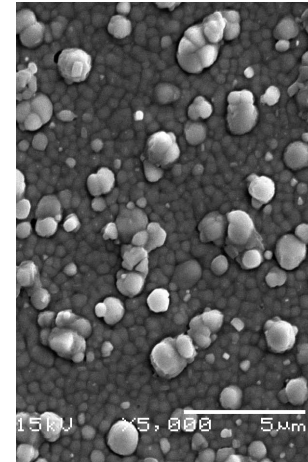
$$R = 1.0 \text{ n}\Omega$$

Influence of kind of REBCO

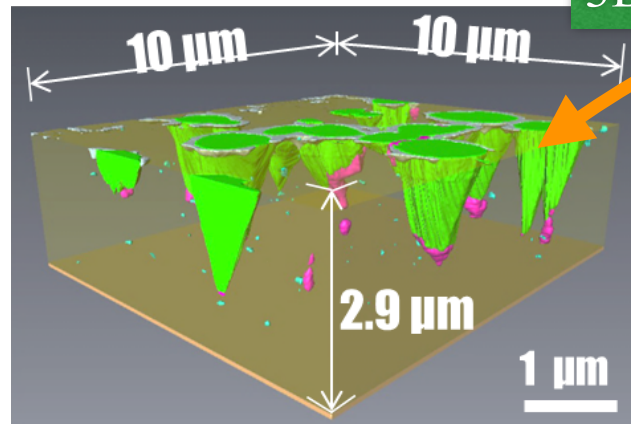
GdBCO
(thickness $\sim 1.2 \mu\text{m}$)



EuBCO
(thickness $\sim 1.2 \mu\text{m}$)



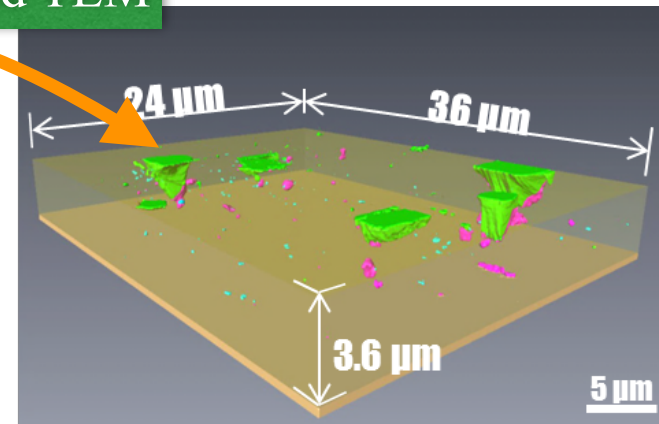
GdBCO



3D slice images obtained TEM

Outer-growth Grains
/ Secondary phase

EuBCO



It was reported the oxygen deficiency at
outermost surface on GdBCO.

Watanabe, et al. Physics Procedia 45 (2013) 165.

Kaneko et al. (Kyushu unit)

The jointing resistance not only depends on the surface morphology of REBCO.

Summary

We developed low temperature jointing in air.

Jointing by Au nano-pastes

&

Jointing by Ag nano-pastes

Handy & post-O₂ annealing-free

150°C, 1h in air

Low jointing resistance

1.0 nΩ (10mmW-160mmL)

In the case of good surface condition

Tensile strength > 1 kN

> 1kN

You can joint on the hot plate!

The jointing resistivities in the different REBCO were not same.

The possibilities of contributing to the resistivity as follows,

**Outer-growth Grains and/or Secondary phase
Oxygen deficiency at outermost surface**



Comparison of jointing techniques

Method	Resistance	Tensile strength	Jointing atmosphere	Jointing temperature	O ₂ -annealing
Solder joint [*1]	50 ~ 100 nΩ	800 N	Air	~ 220°C	Unnecessary
Diffusion joint of silver layer [*2]	6 ~ 10 nΩ	~ 1 kN	O ₂	300 ~ 400°C <i>I_c</i> degradation	~ 12 hours
Superconducting joint [*3]	0 Ω	Unknown	O ₂	800 ~ 850°C <i>I_c</i> degradation	post annealing / long slow cooling
Nano-particle pastes joint	~1 nΩ	> 1kN	Air	~ 150°C	Unnecessary

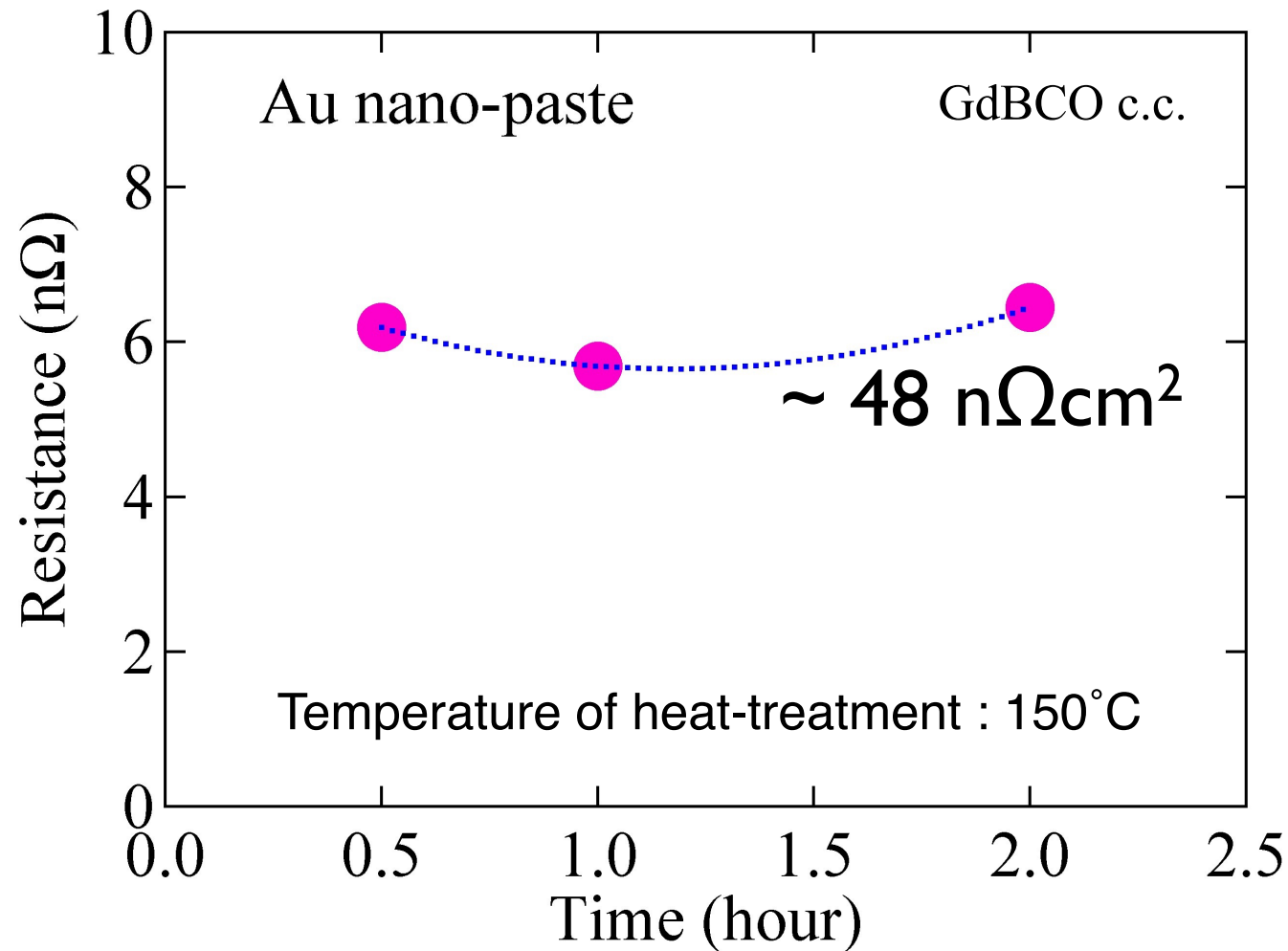
Present work



***Thank you for your
attention !***

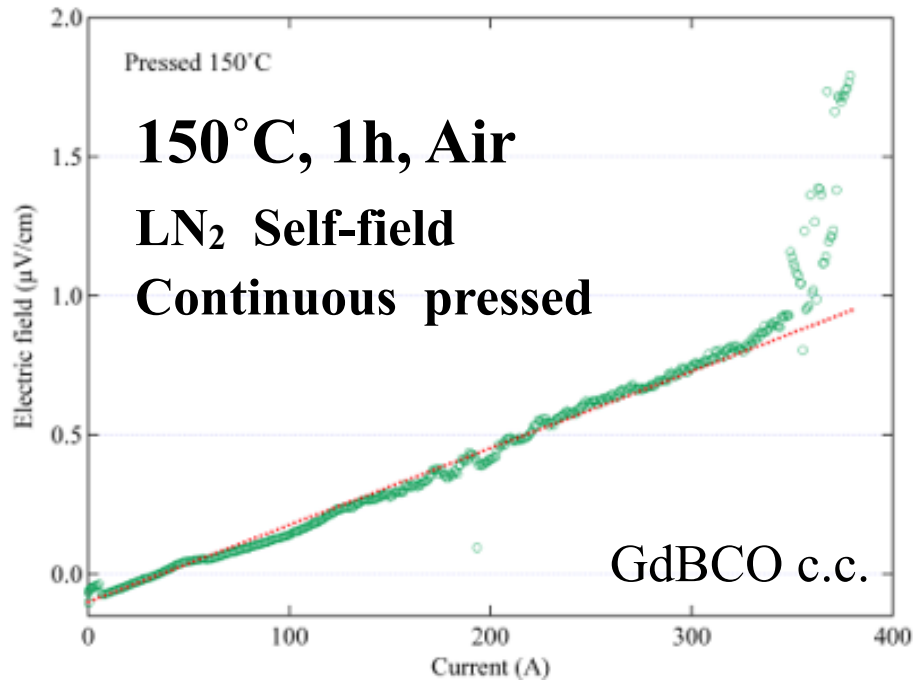
We are special thanks to Dr.T. Kato of JFCC.

Results (Heat-treatment period versus resistance)



The minimum resistance was obtained with heat treatment time of about 1 hour.

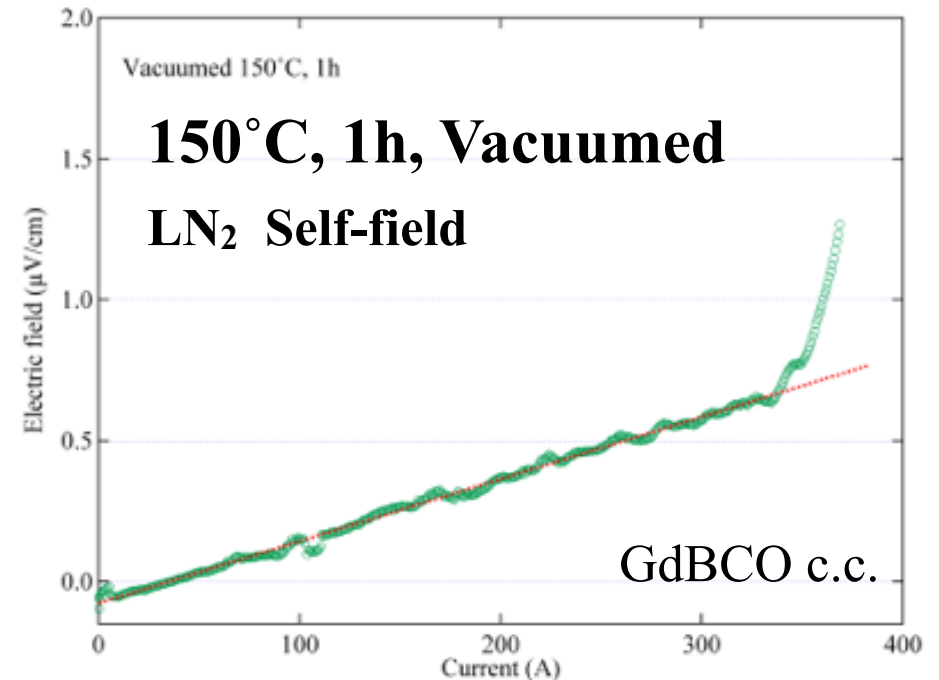
Trial of decrease the vacant space by pressing and vacuuming



Sheet resistivity
48 nΩ • cm²



Continuous pressing
52 nΩ • cm²



Sheet resistivity
48 nΩ • cm²



Vacuuming by rotary pump
40 nΩ • cm²

Vacuuming was slightly effective to decrease resistivity.

Preliminary work :However, there was not so much difference.

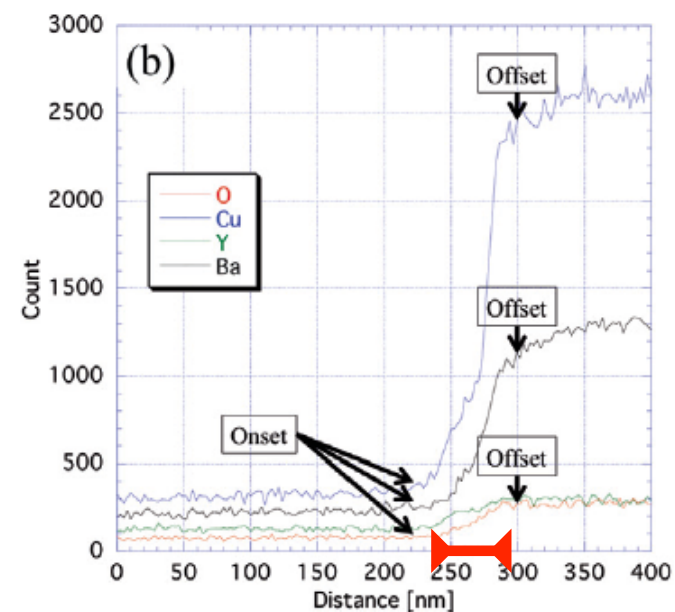
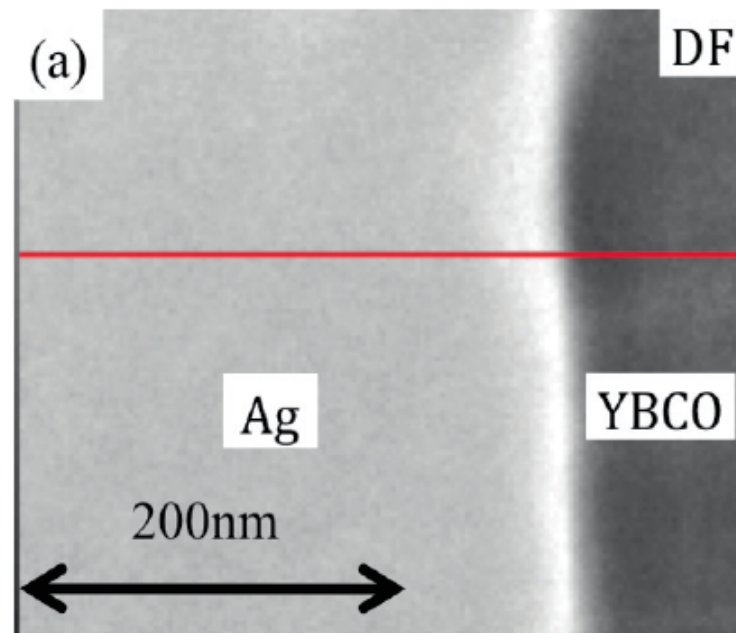
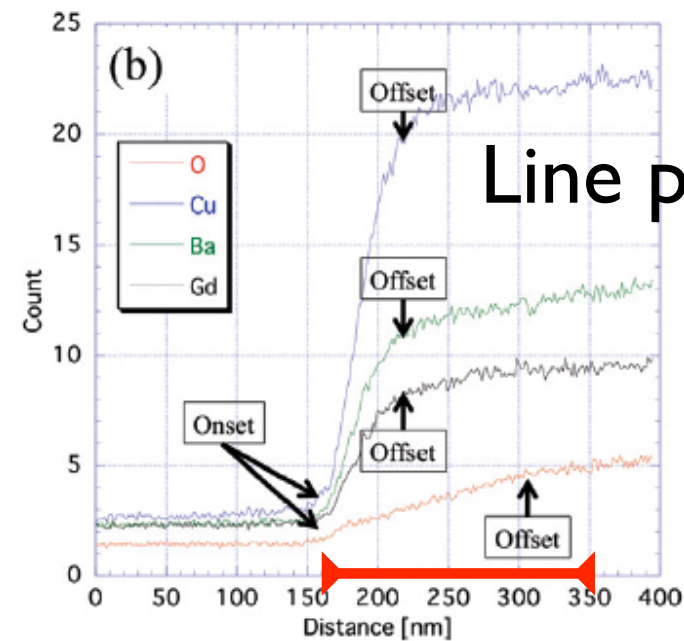
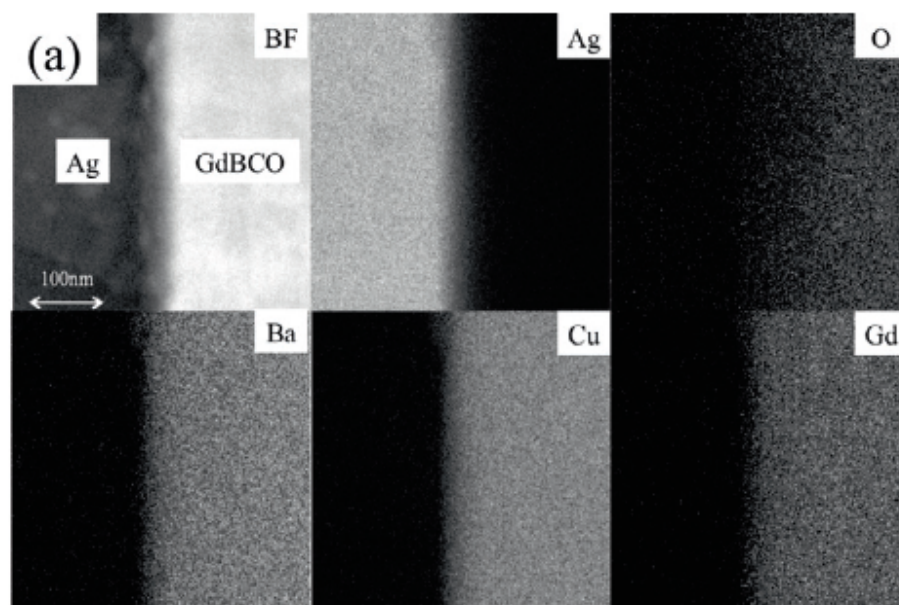
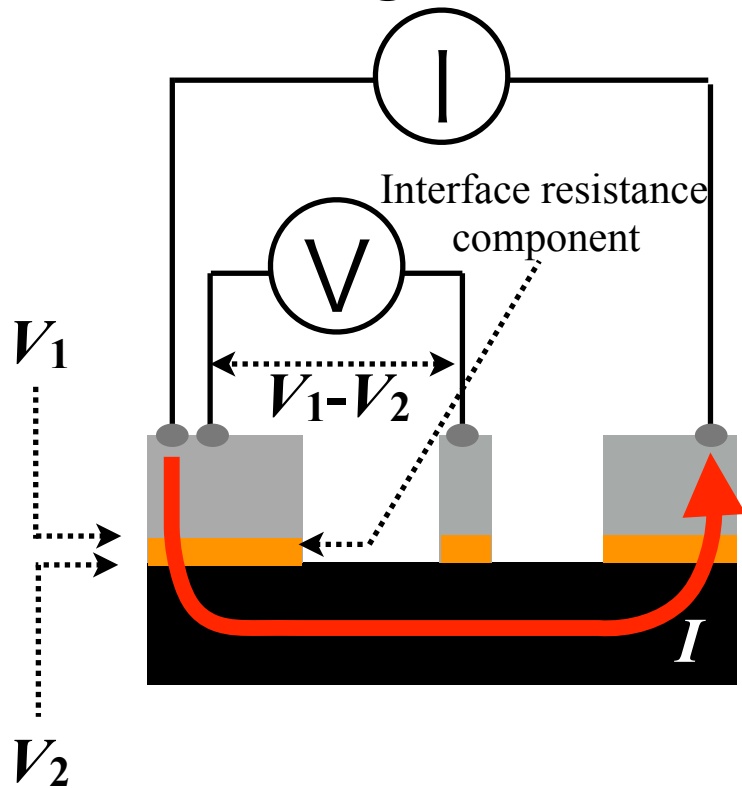


Fig. 2. STEM dark field image (a). EDS line-profile (b)

Study of factors in joint resistance for GdBCO coated conductors
 Physics Procedia 45 (2013) 165 – 168
 T. Watanabe^a, T. Kamata^a, T. Maebatake^a, R. Teranishi^{a*}, T. Kiss^a, K. Yamada^a,
 K. Kaneko^a, M. Yoshizumi^b, T. Izumi^b

Measuring of the interface resistance

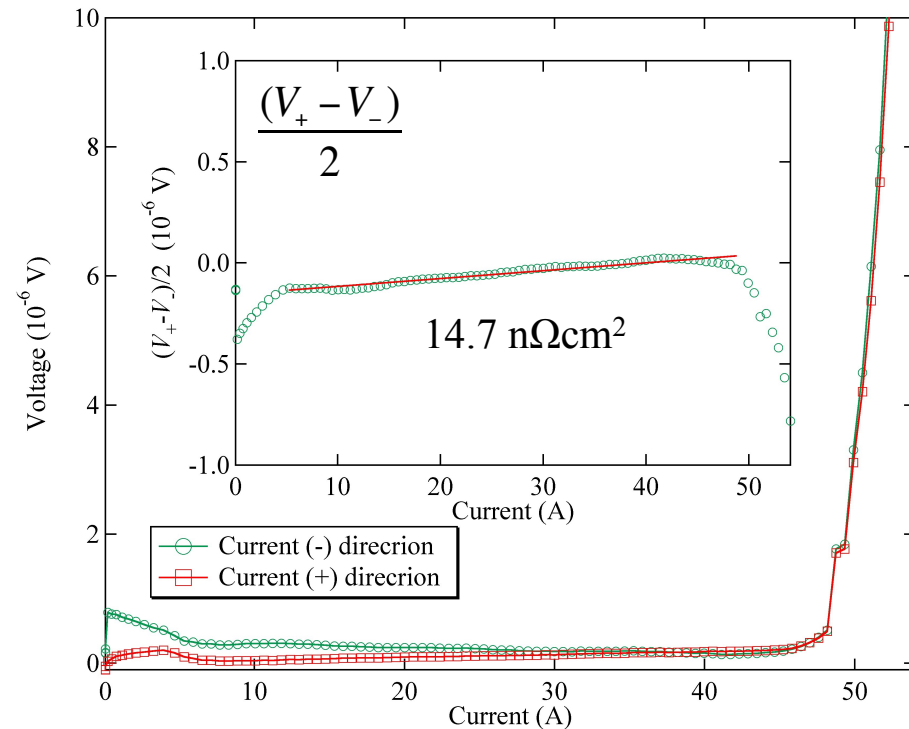
EuBCO
(thickness $\sim 0.5 \mu\text{m}$)



Since the internal resistance of the voltmeter is large, no current flows through the voltage terminal.

Thermal electromotive force was canceled by current reversal.

The voltage at which interface resistance occurs is $V_1 - V_2$.



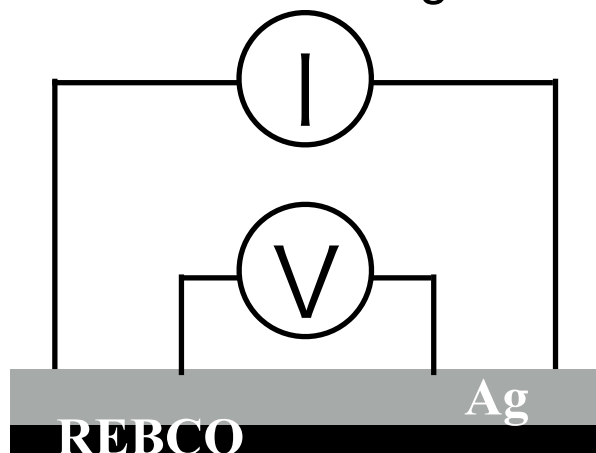
Sheet resistivity = $14.7 \text{ n}\Omega\text{cm}^2$

It is assumed that the jointing resistance is mainly the interface resistance.

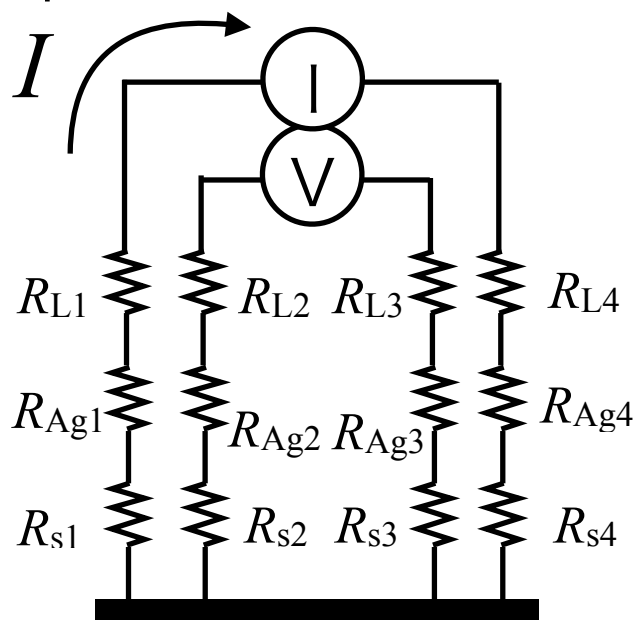
$14.7 \text{ in } 19 \text{ n}\Omega\text{cm}^2$ was the interface resistivity.

Reference data

Four terminal configuration



Equivalent circuit



$R_{s1\sim4}$: Interface resistance (Ag - REBCO)

$R_{Ag1\sim4}$: Ag

$R_{L1\sim4}$: lines

thermal electromotive force (independent on current direction)

Evaluation of generated resistance

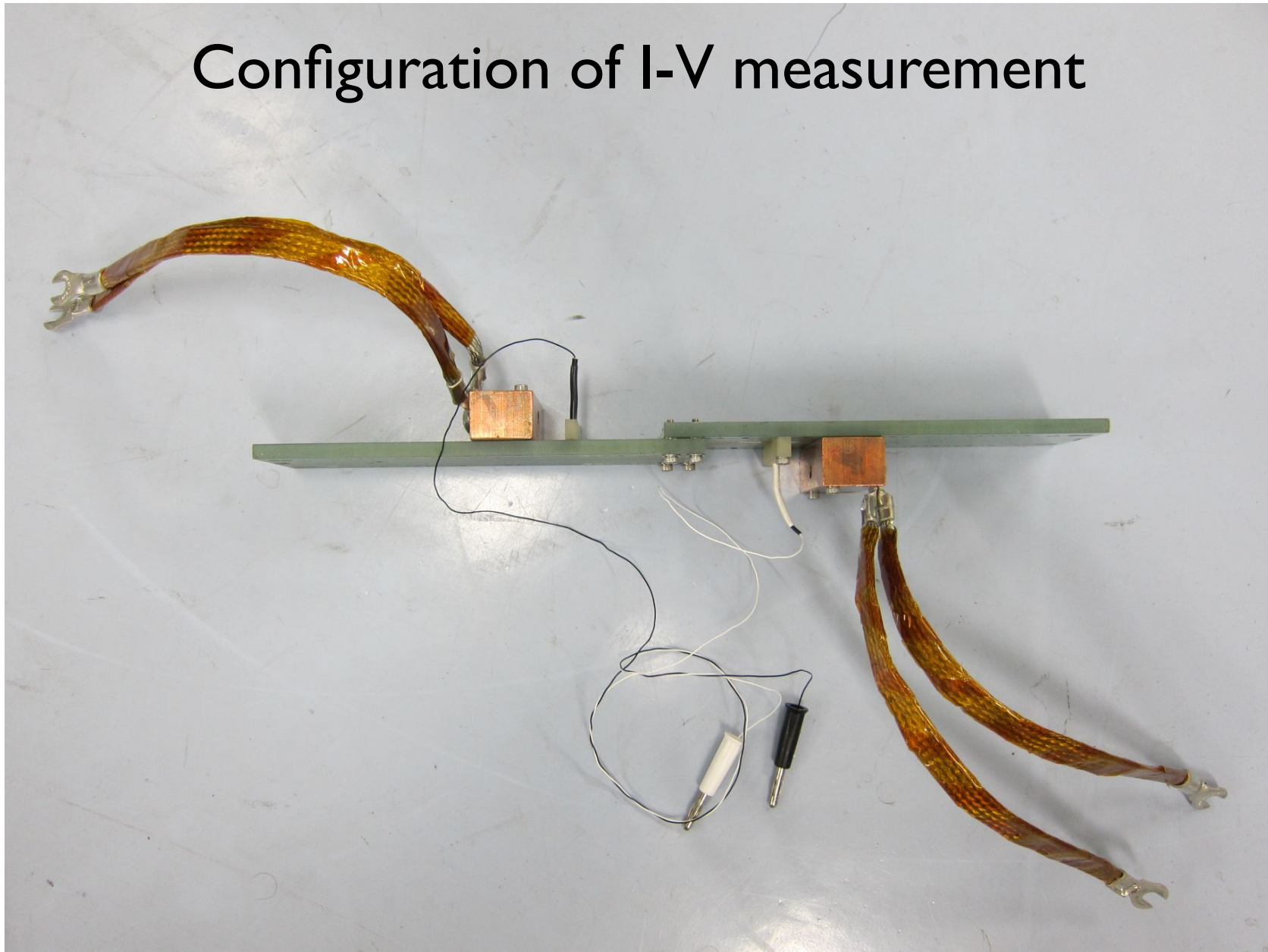
Metal	Resistivity @ 77K (Ωm)	Resistance (30mm^2 , thickness = $8\mu\text{m}$)
Au	5.0×10^{-9}	2.08 p Ω
Ag	3.0×10^{-9}	1.25 p Ω
Cu	2.5×10^{-9}	1.04 p Ω

Resistances of Au, Ag, Cu are negligible compared to jointing resistance (n Ω order).

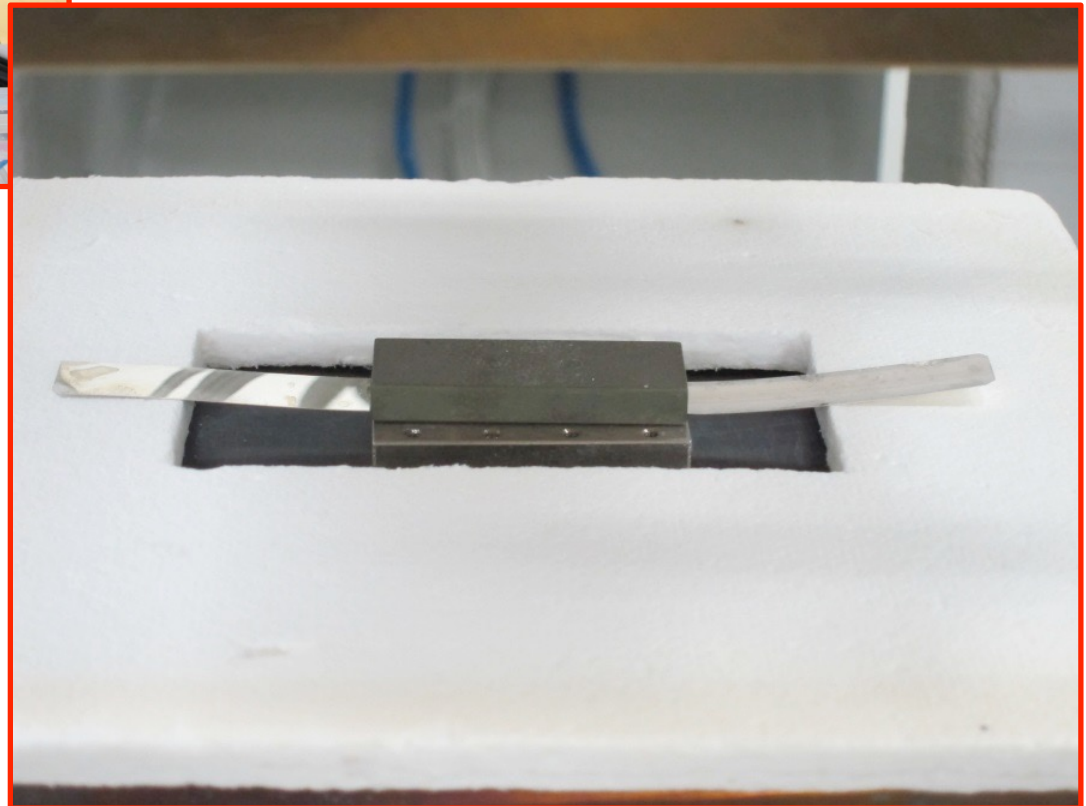
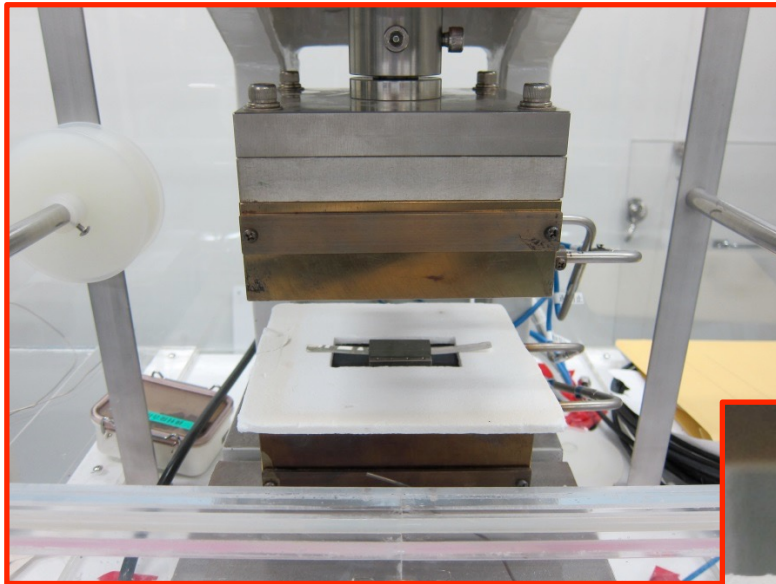
It is necessary to know the interface resistance between Ag and REBCO surface.

How to measure it?

Configuration of I-V measurement



Continuous pressing by hot-press



**It is considered that the solvent and the dispersant
vaporize to generate voids**



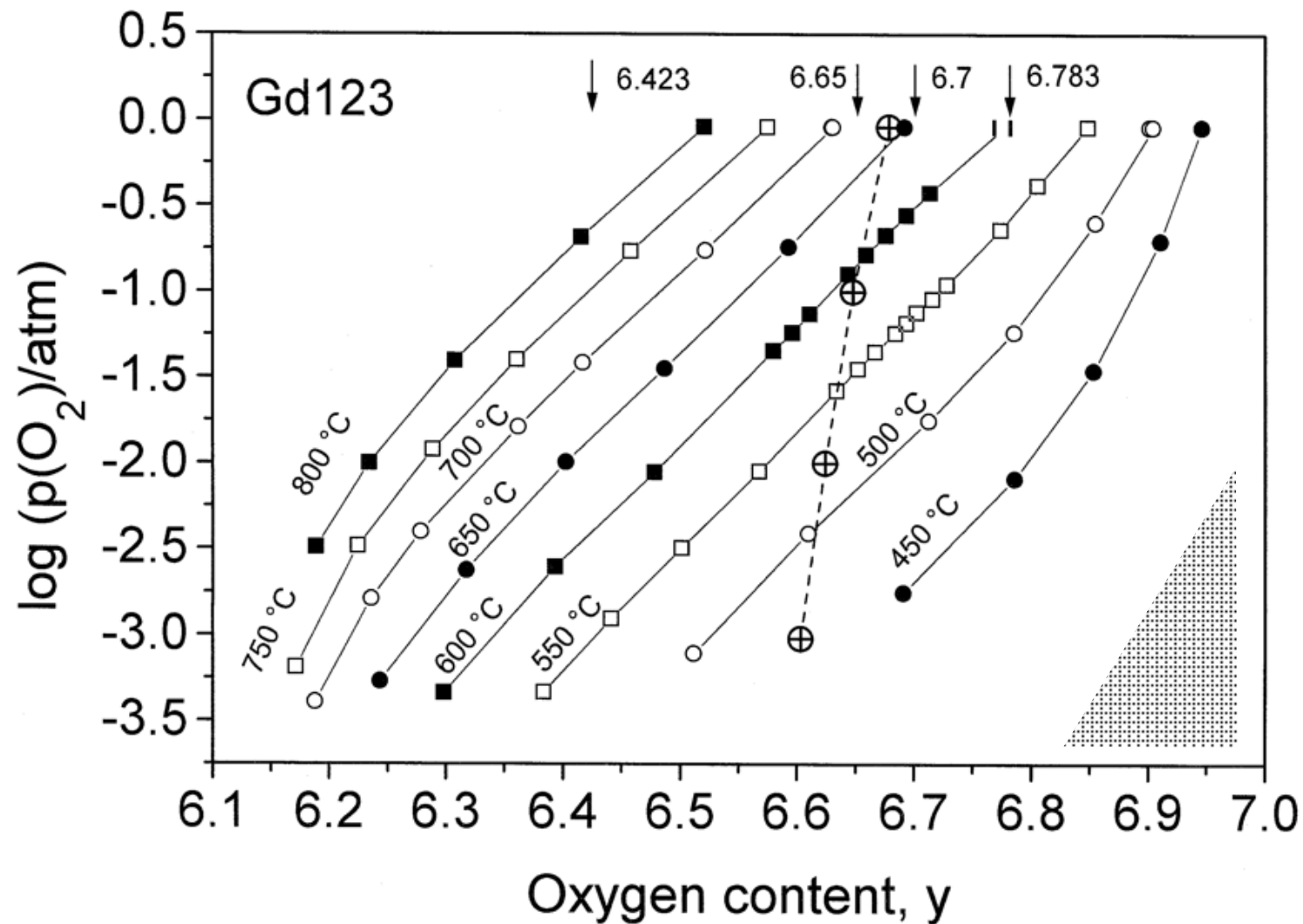
Possibility of widening of the gap by pressurization



**Possibility that components vaporized by
decompression were discharged to the outside**

Reference data

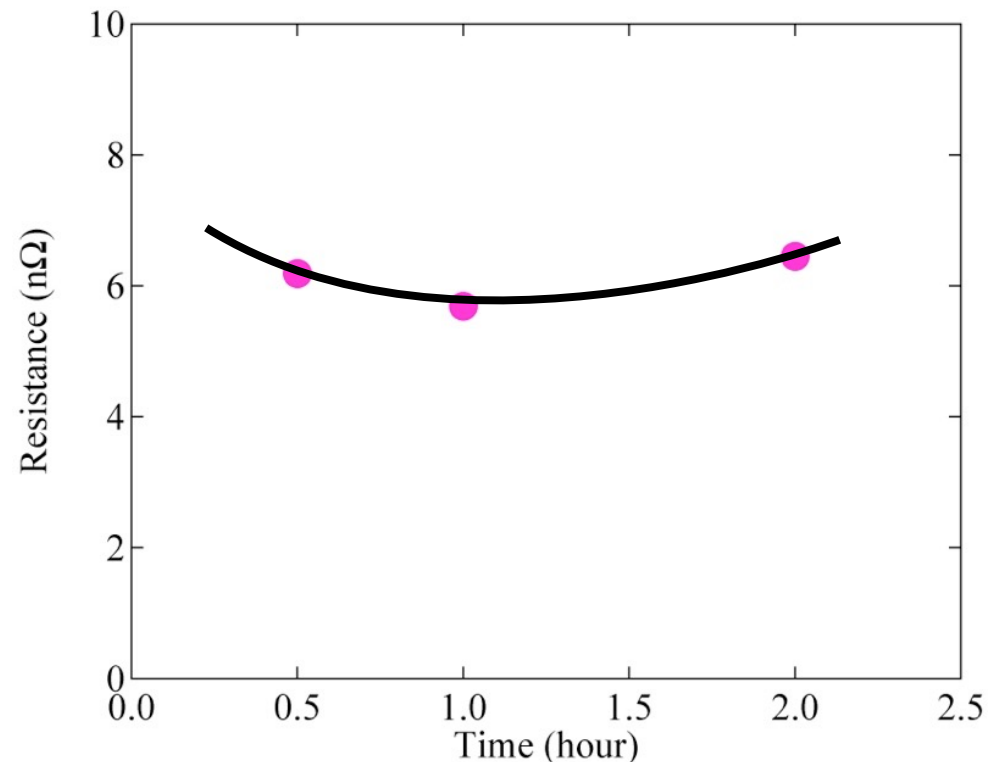
F. Prado et al. Physica C295 (998)235.



Reference data

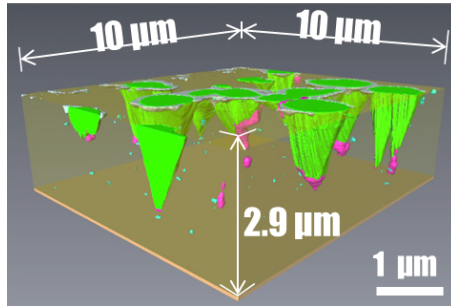
Period dependence@150°C

- Jointing
 - Are 1cm-w × 8cm-L
 - Pressure ~50MPa
 - Treatment temperature 150°C
 - Time 0.5, 1.0, 2 h

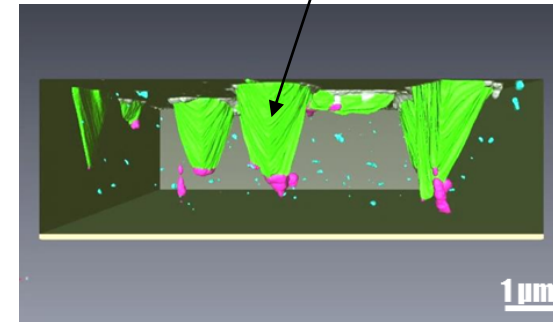


Three dimensional slice images obtained from TEM

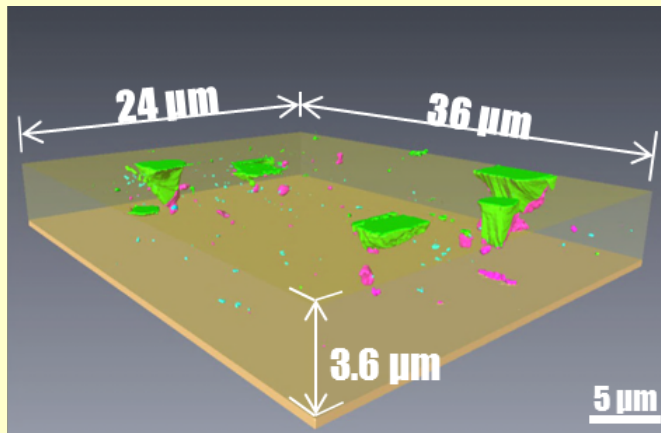
GdBCO-BHO (3.5mol%)



■ : Outer-growth grains
■ : CuO



EuBCO-BHO (3.5mol%)



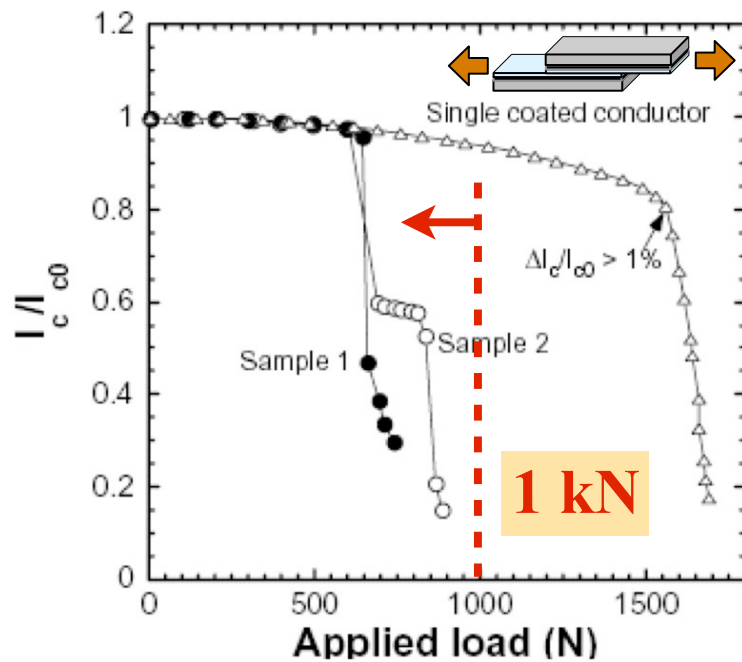
*Lower Ratio of
“Outer-growth Grains”*

*Lower Possibility of
Outer-growth Grains on CuO*

Tensile strength

Solder joint

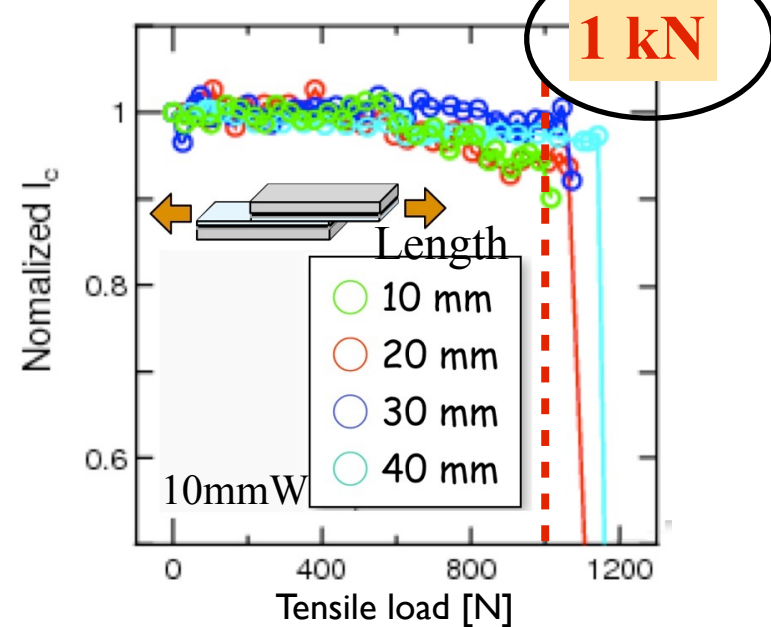
M. Sugano *et al.*,
(2006)ASC 2006.



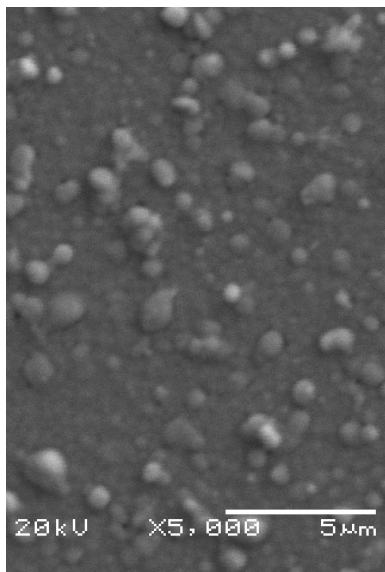
Diffusion jointing of silver layer

J.Y. Kato, *et al.*, Physica C445-448(2006)686.

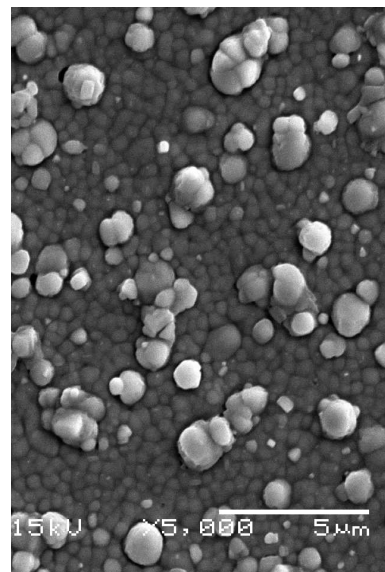
An example of diffusion jointing of silver layer



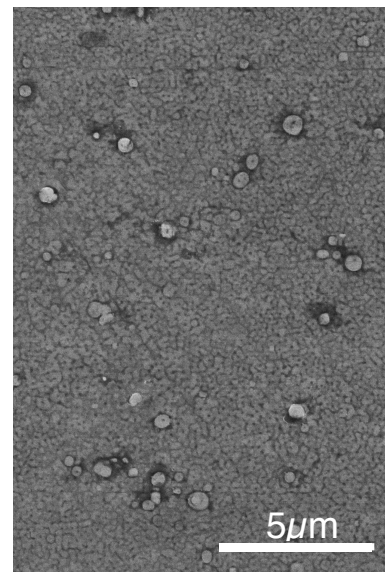
GdBCO
(thickness $\sim 1.2\ \mu\text{m}$)



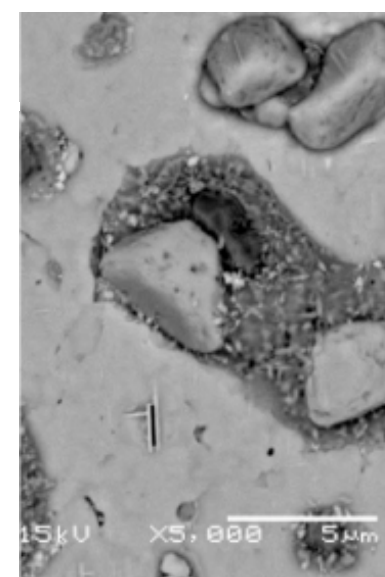
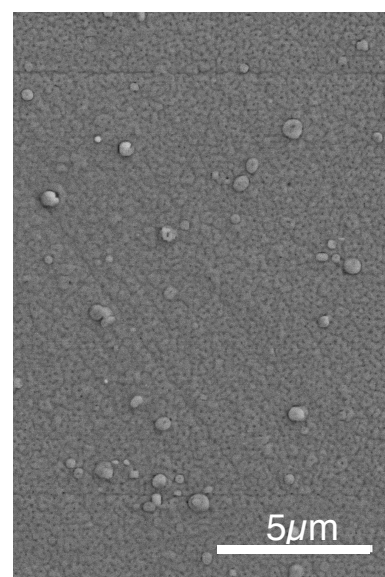
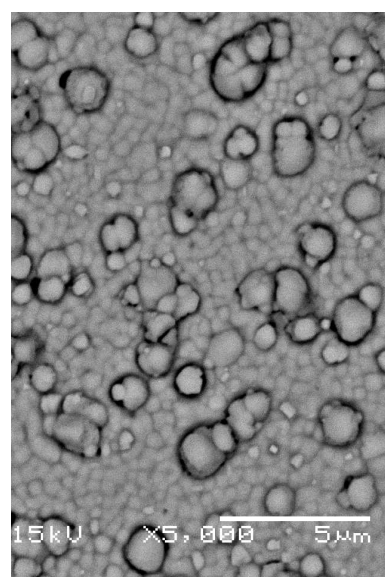
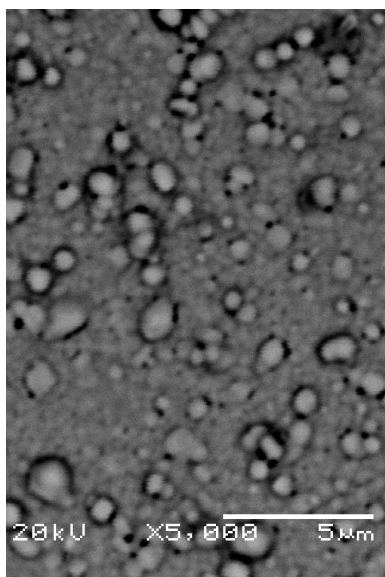
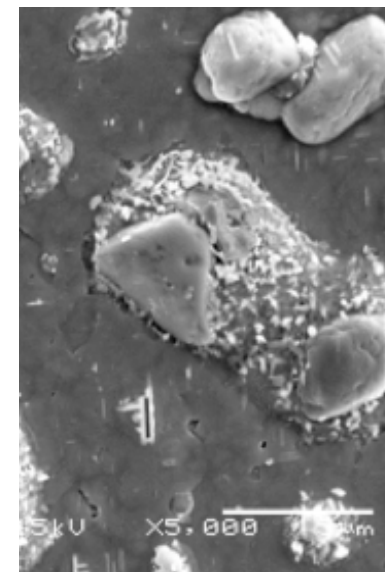
EuBCO
(thickness $\sim 1.2\ \mu\text{m}$)



EuBCO
(thickness $\sim 0.5\ \mu\text{m}$)



EuBCO+BHO
(thickness $\sim 3.6\ \mu\text{m}$)



$48\ \text{n}\Omega \cdot \text{cm}^2$

$16\ \text{n}\Omega \cdot \text{cm}^2$

$19\ \text{n}\Omega \cdot \text{cm}^2$

$78\ \text{n}\Omega \cdot \text{cm}^2$