



Wrocław University of Technology

The Influence of Thermal Process on Electrical Conductivity Microstructures Made by Ink Containing Nano Sized Silver Particles

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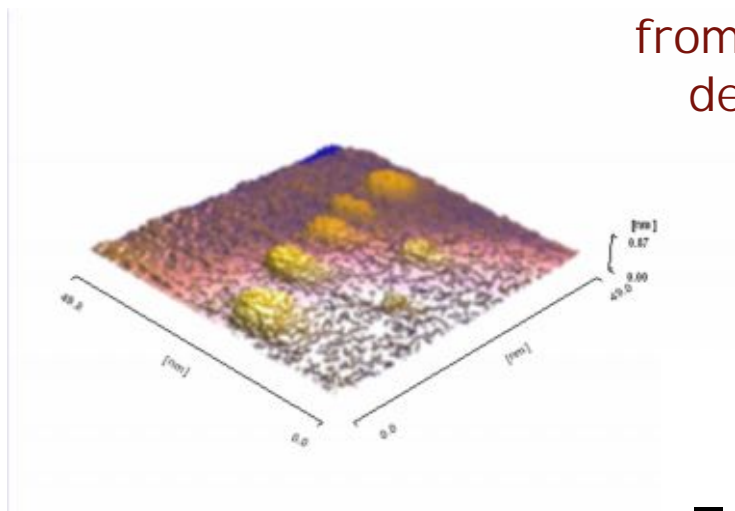
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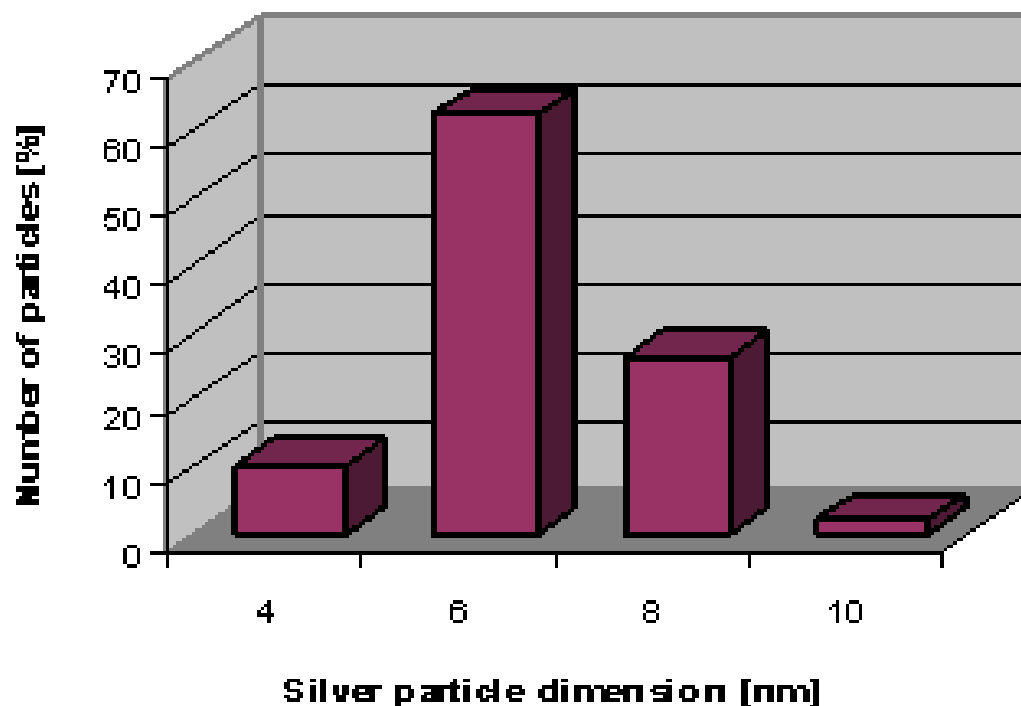


SILVER

from Ag salts of fatty acids during their thermal decomposition in an oxygen-free atmosphere



STM picture



Size distribution

THE INK

Solvent:
tetradecan



Number of components	One
Consistency	Very low viscous fluid
Color	Dark brown to black with metallic shine
Percentage of silver filler	~ 50 %
Viscosity ^{*)}	3.6 ÷ 18 mPas
Thixotropy index	~ 1.0
Surface tension value	28.5 ÷ 32.5 mN/m
Specific gravity	1.3 ÷ 1.6 g/cm ³
Electrical resistivity ^{**)}	(1 ÷ 3) 10 ⁻⁵ Ωcm

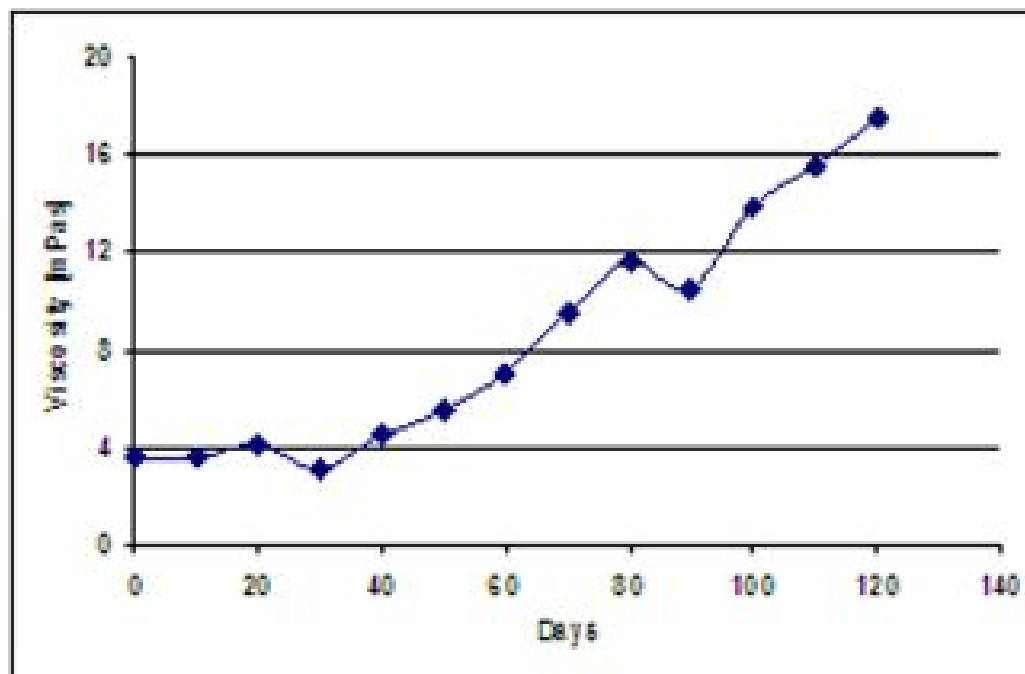
*) Brookfield LVDVII + CP; 100 rpm; 20 °C

***) after 230 °C; 60 min sintering



THE INK

Viscosity



Sedimentation: 0.4 %/20 days

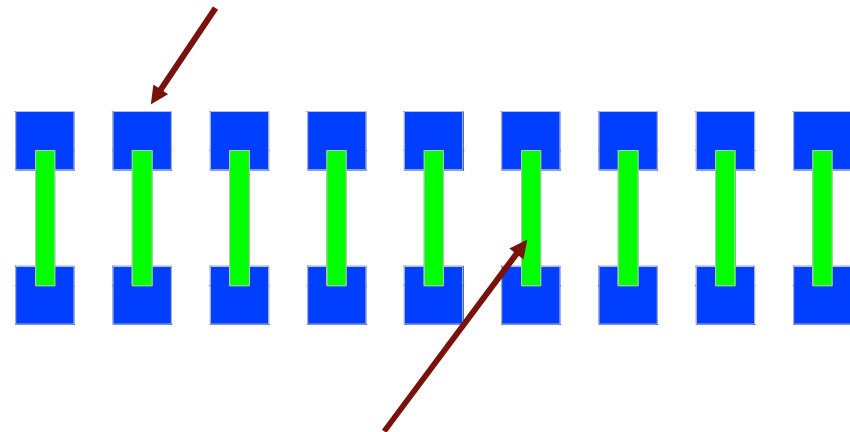
PRINTED STRUCTURES



Dimatix DMP-2831 printer

- 12 Nozzles: 22.5 μm diameter
- Maximum jetting frequency: 5 kHz
- Drops volume: about 10 pl

First step: 9 pairs of contacts (3 x 3 mm) were printed and sintered 1 hour in temperature of 250 °C



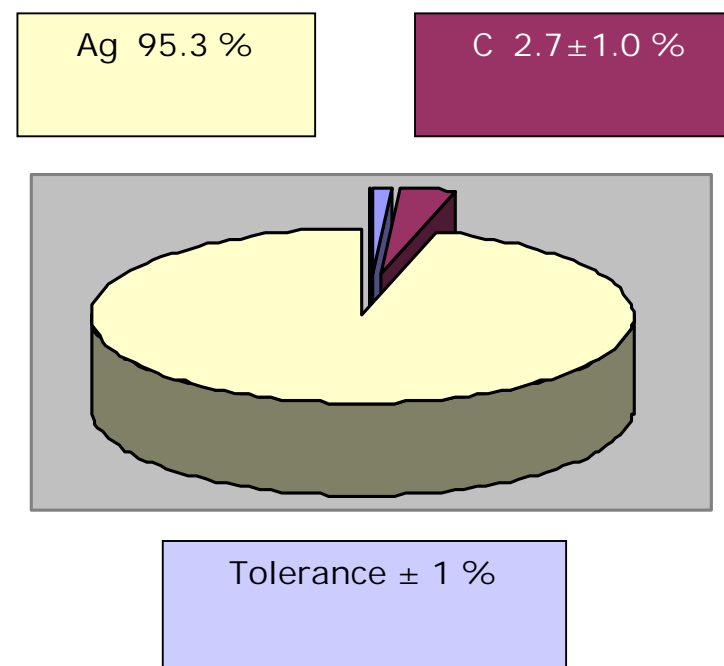
Second step: paths with 1 mm width were printed joining contacts. The distance between contacts: 3.4 mm or 8.8 mm. Structures were drying by a few seconds in temperature of 110 °C



ELECTRICAL RESISTIVITY

JUST AFTER PRINTING: Resistivity $\rightarrow \infty$

Each nAg particle is protected by special chemical „shell”. This „shell” layer was build during nAg production process

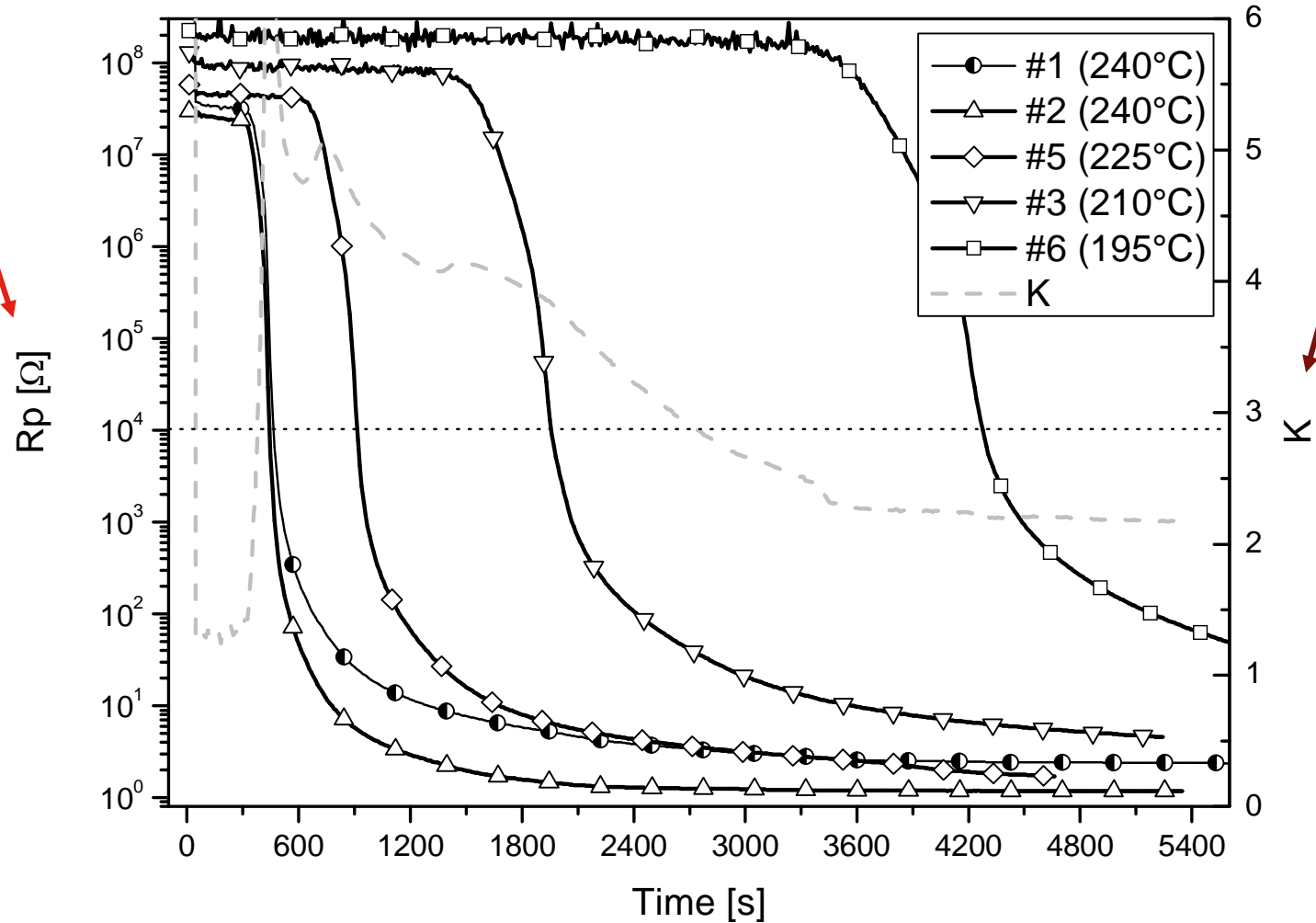




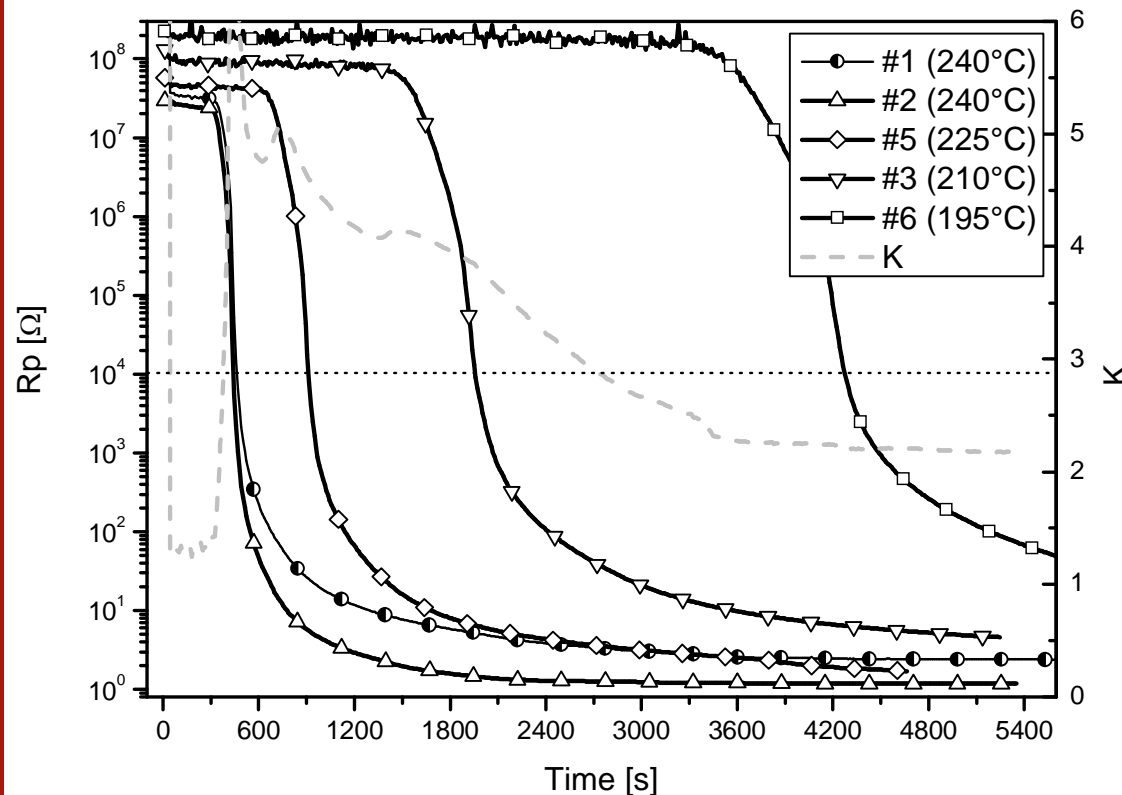
THERMAL PROCESS

Resistance

Factor K : takes into account the influence of measuring system



THERMAL PROCESS



THREE STAGES:

1° - in sintering temperature the high resistance remains stable,

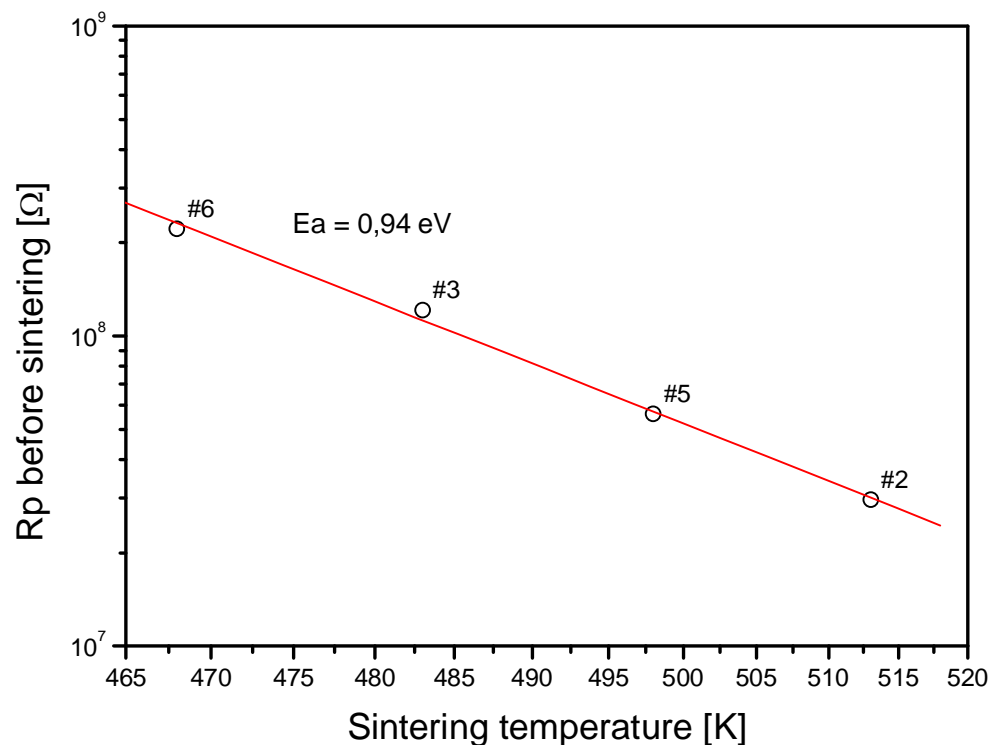
2° - resistance decreases in relatively short period of time,

3° - low resistance changes during the thermal process.

CONCLUSIONS:

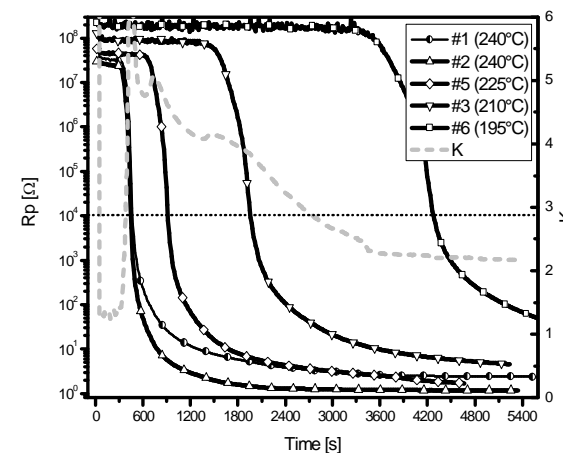
- final resistance is almost the same for the range of 195 °C - 240 °C temperature changes,
- the time of the first stage is much longer with lower temperature.

THERMAL PROCESS



CONCLUSIONS:

- So high activation energies (0.94 eV) may suggest the ionic type of conductance.

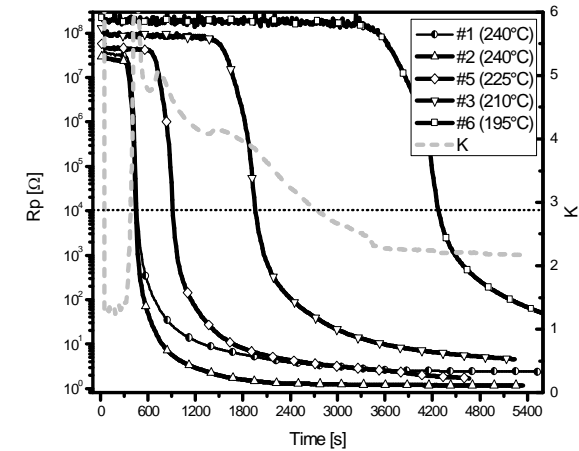
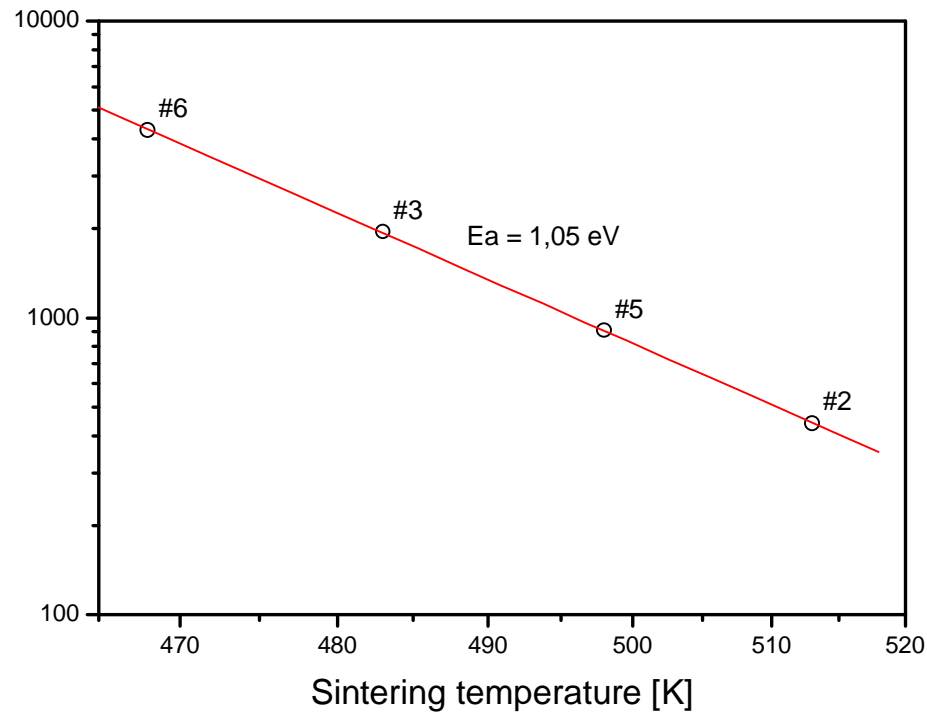


IN THE BEGINNING OF THE SINTERING PROCES:

- the resistance for the same type of samples depends on temperature

THERMAL PROCESS

Sintering time [s]



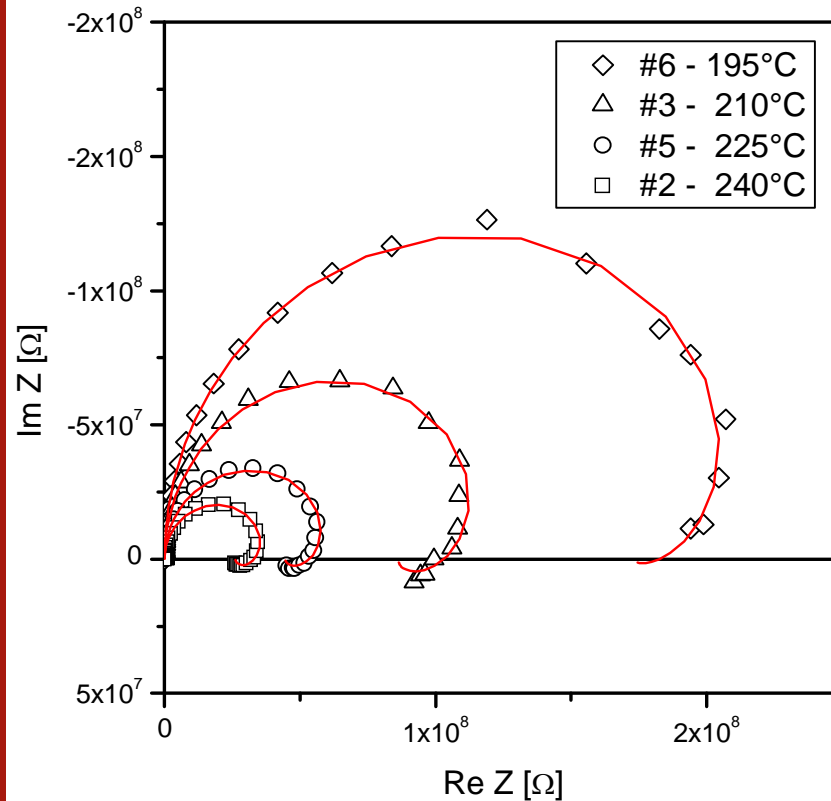
Dependence of sintering time on sintering temperature

$$t = 2,32 \cdot 10^{-8} \exp\left(\frac{1,05 \text{ eV}}{kT}\right) [s]$$

CONCLUSIONS:

➤ The phenomenon of sintering process is consistent with Arrhenius law with activation energy of 1.05 eV. Probably there is a very quick reaction with that activation energy.

THERMAL PROCESS



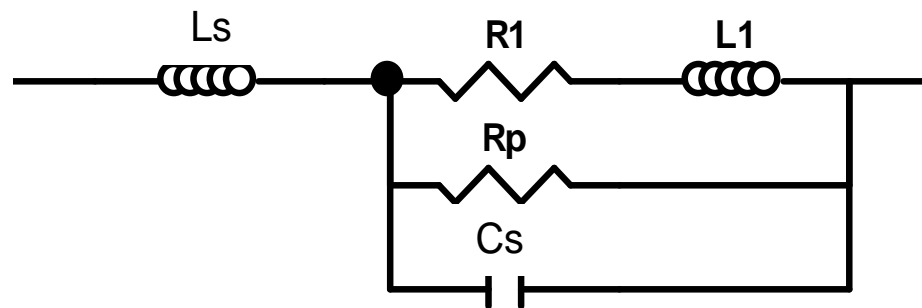
NYQUIST PLOTS of measured samples (real and imaginary parts of impedance are presented):

for short sintering times, the plots pass on positive values imaginary part of impedance

CONCLUSIONS:

➤ It is typical for impedance measurement of an object in with Faradaic process takes place

THERMAL PROCESS



THE EQUIVALENT CIRCUIT (describing experimental plots)

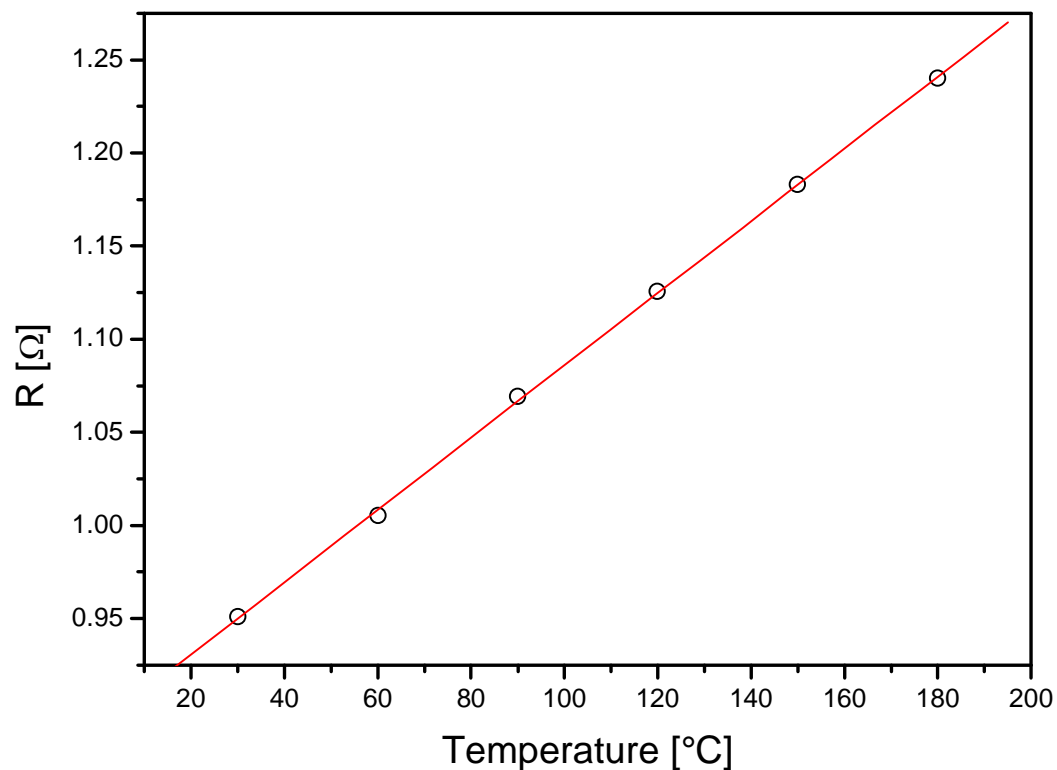
The branch R1-L1 is responsible for the phenomena, while the Rp represents the resistance of the printed structure and both Ls and Cs - the self-inductance and self-capacitance of the measurement system.

CONCLUSIONS:

➤ The L1 cannot be treated as real inductance. It is caused by the reactions which output is the same as "normal" inductance, but in fact it is not connected with energy storage. Along with starting the second stage of sintering process (sudden drop of resistance value), the R1 - L1 branch disappears



AFTER THERMAL PROCESS



RESISTANCE VALUE
DEPENDS ON OPERATION
TEMPERATURE

CONCLUSIONS:

➤ This is typical metallic type of conductance with temperature coefficient of resistance equal 2080 ppm/K. It is lower value than for bulk silver (3800 ppm/K).



CONCLUSSIONS

TO OBTAIN GOOD ELECTRICAL CONDUCTIVITY, THE PRINTED STRUCTURES NEEDS ADDITIONAL ENERGY, MAINLY DURING A HEATING PROCESS. IT IS SHOWN, THAT THERMAL PROCESS INFLUENCES STRONGLY THE RESISTANCE ON THE PRINTED STRUCTURES AND DIFFERENT PHENOMENA TAKE PLACE DURING THIS SINTERING PROCESS:

- ON THE BEGINNING OF THE HEATING, THE REACTION WITH ACTIVATION ENERGY OF 1.05 eV IS OBSERVED; THE HIGHER TEMPERATURE CAUSES LOWER RESISTANCE,
- DURING THE HEATING PROCESS, THE STABLE, VERY HIGH RESISTANCE VALUE STAYS THE LONGER, THE TEMPERATURE IS LOWER, - THE PROCESS OF RESISTANCE DECREASING IS RELATIVELY SHORT, BUT RECEIVING THE FINAL CONDUCTANCE NEED ADDITIONAL TIME IN WHICH THE RESISTANCE DECREASES SLOWLY,



CONCLUSIONS

TO OBTAIN GOOD ELECTRICAL CONDUCTIVITY, THE PRINTED STRUCTURES NEEDS ADDITIONAL ENERGY, MAINLY DURING A HEATING PROCESS. IT IS SHOWN, THAT THERMAL PROCESS INFLUENCES STRONGLY THE RESISTANCE ON THE PRINTED STRUCTURES AND DIFFERENT PHENOMENA TAKE PLACE DURING THIS SINTERING PROCESS:

- THE PHENOMENON OF SINTERING PROCESS IS CONSISTENT WITH ARHENIUS LAW WITH ACTIVATION ENERGY OF 1.07 eV,
- THE IMPEDANCE ANALYSIS SUGGESTS THE OXIDATION CHEMICAL REACTION DURING THE SINTERING PROCESS,

AFTER SINTERING PROCESS, THE CONDUCTIVE STRUCTURES HAVE IS TYPICAL METALLIC TYPE OF CONDUCTANCE WITH TEMPERATURE COEFFICIENT OF RESISTANCE EQUAL 2080 ppm/K.