Nonlinear Resistors
Resistance effect in polycrystalline metallic oxide (ceramics)

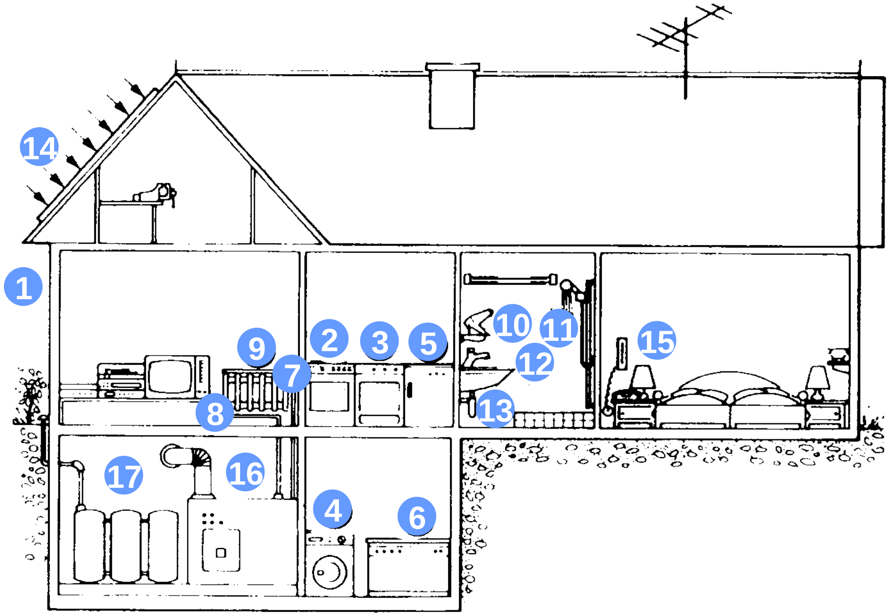
Type	Physical effect	Materials
Temperature-dependent resistance (Thermistor)*		
• Negative Temperature Coefficient (NTC)	**hopping-conduction in metallic oxide**	**spinel, e.g. $(Ni,Mn)_3O_4$** $\sigma \approx 10^{-2}$ $(\Omega\text{-m})^{-1}$
• Positive Temperature Coefficient (PTC)	**grain boundary phenomena in semiconducting ferroelectrics**	**n-doped $BaTiO_3$** $\sigma \approx 10^{2}...10^{3}$ $(\Omega\text{-m})^{-1}$
Voltage-dependent resistance (Varistor)*	**grain boundary phenomena in semiconducting ceramics**	**SiC** **n-doped ZnO**

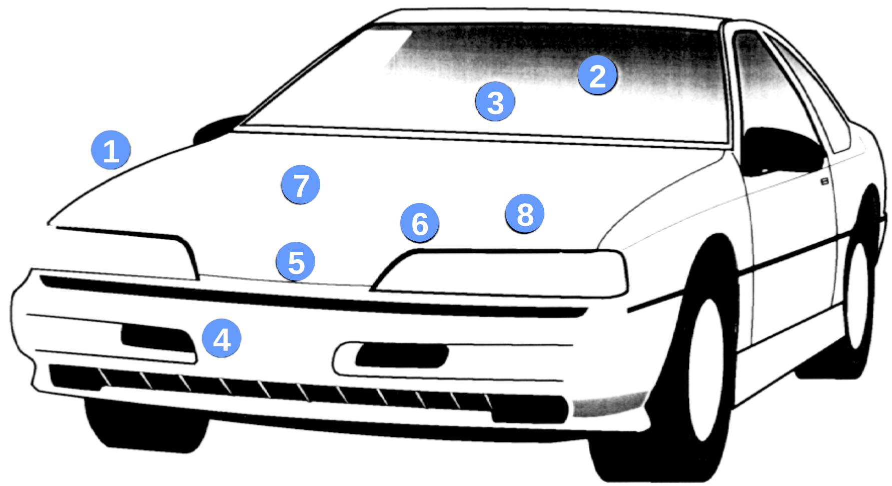
*** Thermistor:** **<u>therm</u>al sensitive res<u>istor</u>**

Varistor: **<u>vari</u>able res<u>istor</u>**

Nonlinear Resistors / NTC
Application of Negative Temperature Coefficient Resistors

- **Temperature measuring and controlling**

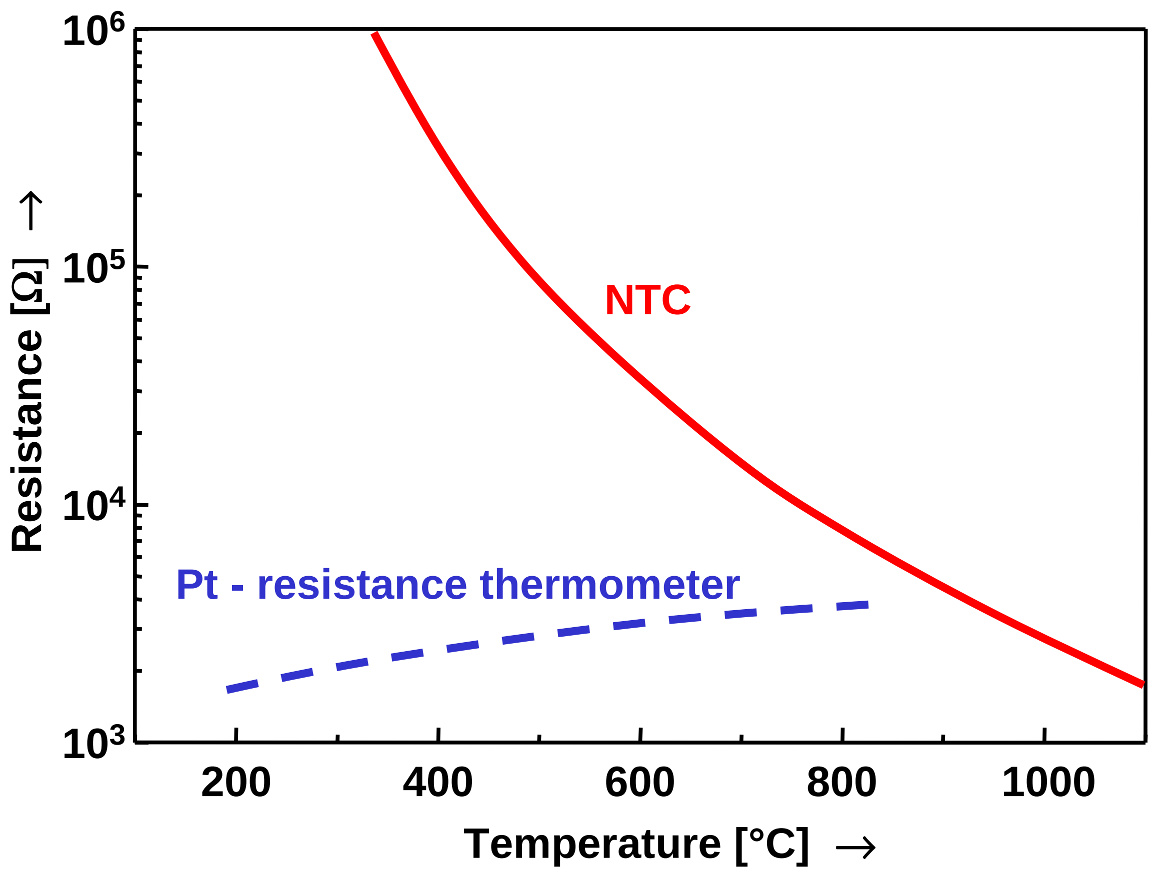




1. Outside/inside temperature
2. Electric cooker
3. Dishwasher
4. Washing machine
5. Refrigerator
6. Freezer
7. Room heater
8. Underfloor heater
9. Storage heater
10. Hand dryer
11. Dryer hood
12. Hair blower
13. Warm water heater
14. Solar heater
15. Clinical thermometer
16. Lamp starter
17. Switch-on current limitation (small motor, circuit divider)

1. Outside temperature
2. Inside temperature
3. Air conditioner
4. Air intake
5. Cooling water
6. Motor oil
7. Transmission oil
8. Brake fluid

Nonlinear Resistors / NTC
Resistance - temperature Characteristic Curve of NTC



Example:

high temperature NTC

range of use: up to 1000 °C

Material:

metallic oxide

The temperature-dependent electric conductivity will be determined by the charge carrier mobility:

$$\mu_n = \frac{K_1}{T} \cdot e^{-\frac{W_A}{kT}}$$

K_1: constant
W_A: activation energy

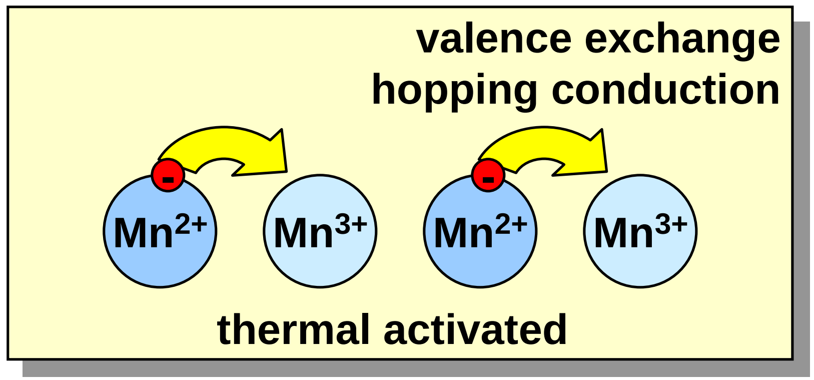
Nonlinear Resistors / NTC
Polycrystalline Semiconducting Metallic Oxide as NTC

Materials: Metallic oxide e.g. Mn, Fe, Co, Ni, Cu, Zn (transition metals)

Bond type: predominantly or partially heteropolar (ionic) bond (metal: cation, oxygen: anion)

Semiconducting properties can result from valence exchange of the cations in the oxide. charge transport through hopping-mechanism (valence „transfer “)

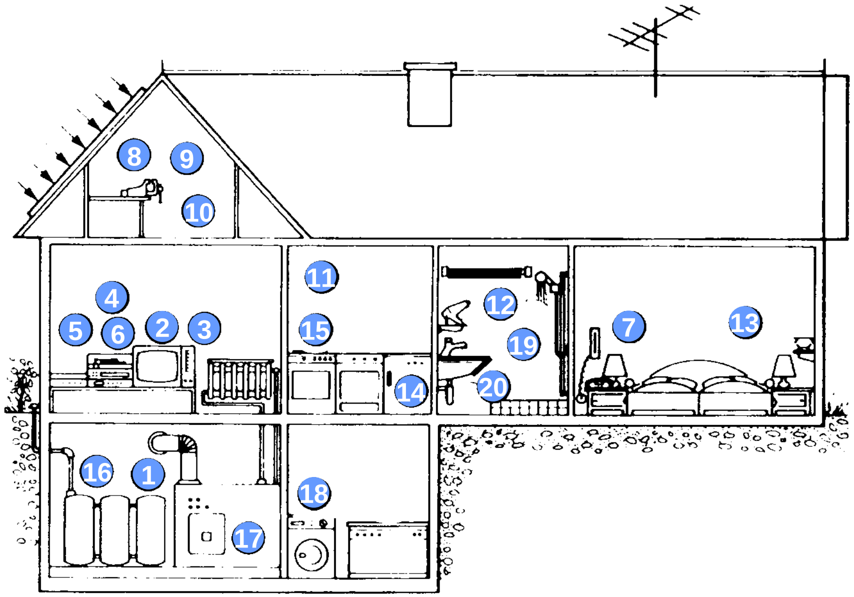
element:	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
valence:		+2	+2	+2	+2	+2	+2	+2	+2
	+3	+3	+3	+3	+3	+3	+3		
	+4	+4	+4	+4	+4				
		+5							

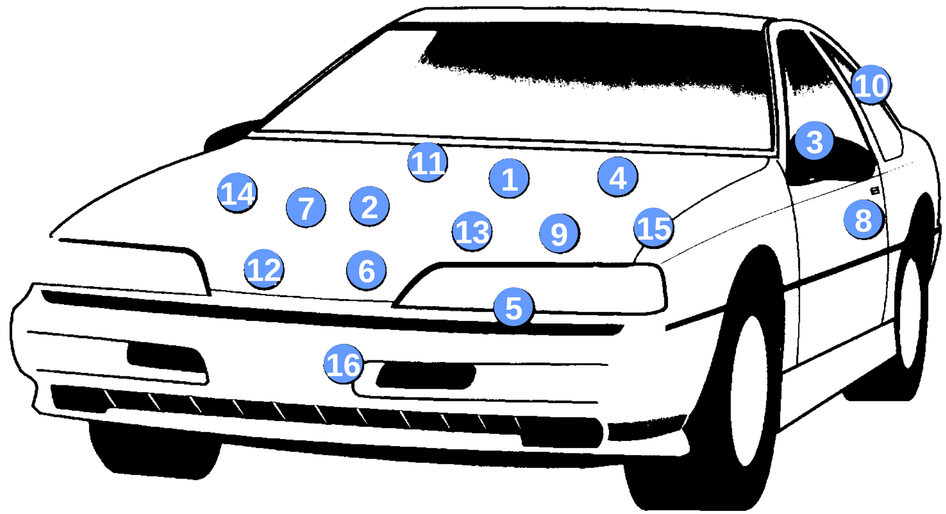


Lattice structure: $A^{2+} B^{3+}_2 O^{2-}_4$ (spinel)

typical NTC: $Ni^{2+} Mn^{3+}_2 O^{2-}_4$

Nonlinear Resistors / PTC
Applications of Positive Temperature Coefficient Resistors

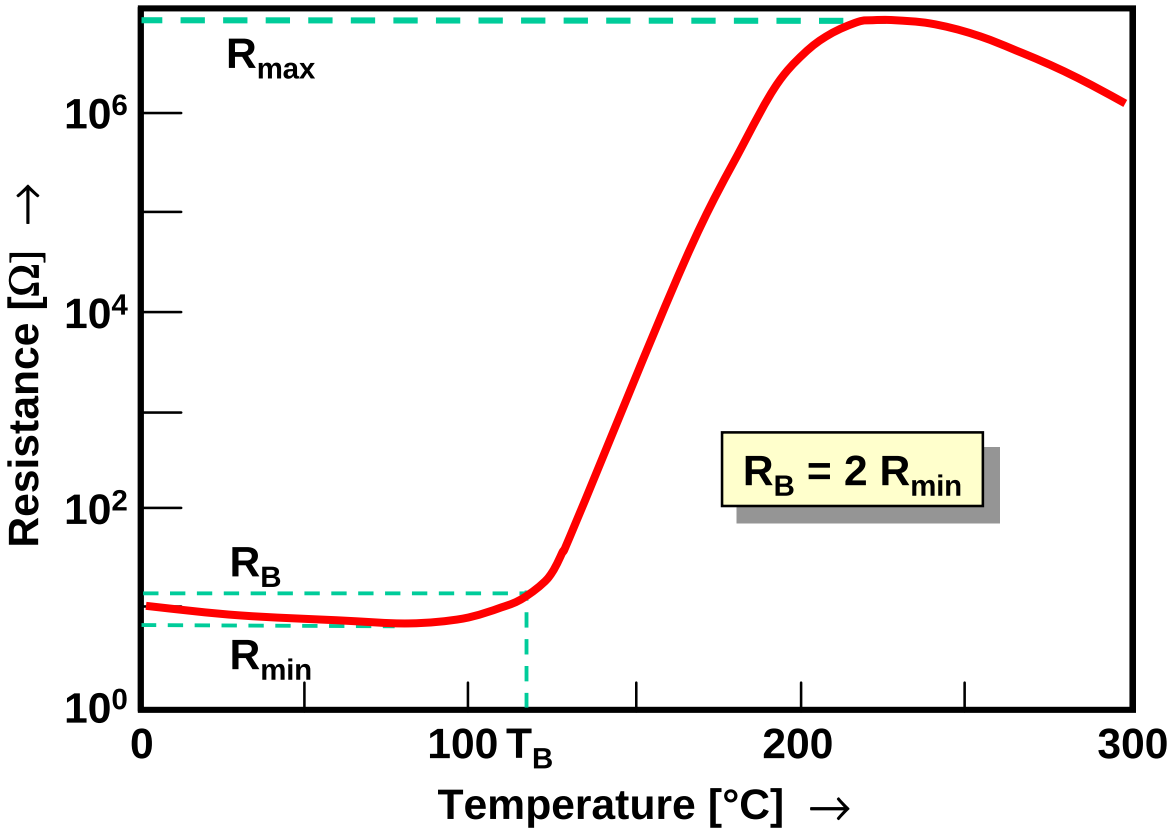




1. Lamp protection
2. TV-demagnetizing
3. Switching power supply overload protection
4. Video overload protection
5. Loudspeaker protection
6. Switching power supply startup
7. Telephone over-current protection
8. Sticking pistol
9. Styrofoam cutter
10. Voltage tester
11. Overload protection for small motors
12. Curls rolling rod
13. Insect annihilator
14. Engine start compressor
15. Warm retaining plate
16. Tank overfilling protection
17. Oil preheating
18. Washing machine door locking
19. Hand dryer
20. heater

1. Thermal valve heating
2. Carburetor heating
3. Mirror heating
4. Spray nozzle heating
5. Headlight washing system
6. Preheating of intake air (carburetors)
7. Mixture preheating (injector)
8. Door lock heating
9. Überlastschutz (elec. small motor)
10. Back window ventilation
11. Windshield wiper system check
12. Brake fluid check
13. Oil level check
14. Cooling water check
15. Gasoline display

Nonlinear Resistors / PTC
Resistance - temperature Characteristic Curve of PTC



Material:
semiconducting $BaTiO_3$
(n- i.e. donor doped)

R_{min}, R_{max}:
extreme values of the PTC branch with sign change in temperature coefficients

R_{max}/R_{min}:
available resistance ratio
maximal proportion: 10^7

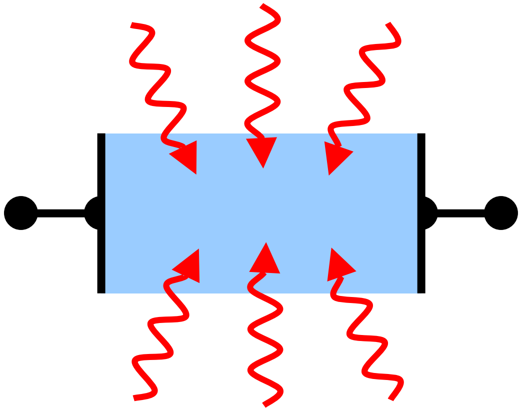
T_B:
reference- or rated temperature of the component at $R_B = 2\ R_{min}$
T_B-values from -30...+250 °C

TK_R: Temperature coefficient of the resistance $TK_R = \frac{1}{R} \cdot \frac{dR}{dT}$, TK_R-values from 0,1...0,3 K^{-1}

Nonlinear Resistors / PTC
Applications

Sensor

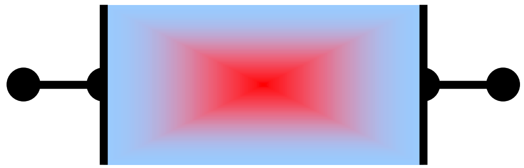
heat from the environment



- **electrical thermometer**
- **temperature rise protection**

Controller

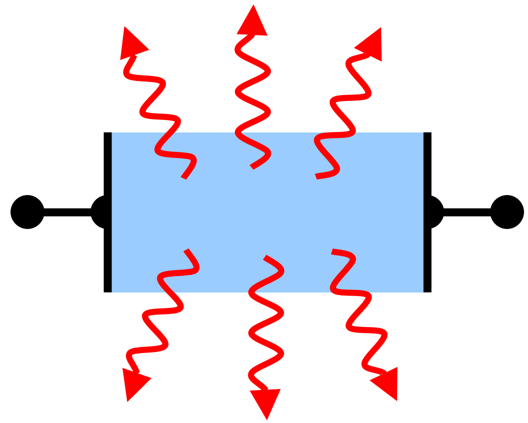
self-heating



- **current stabilization**
- **switch time delay**
- **level monitoring**
- **current measurement**

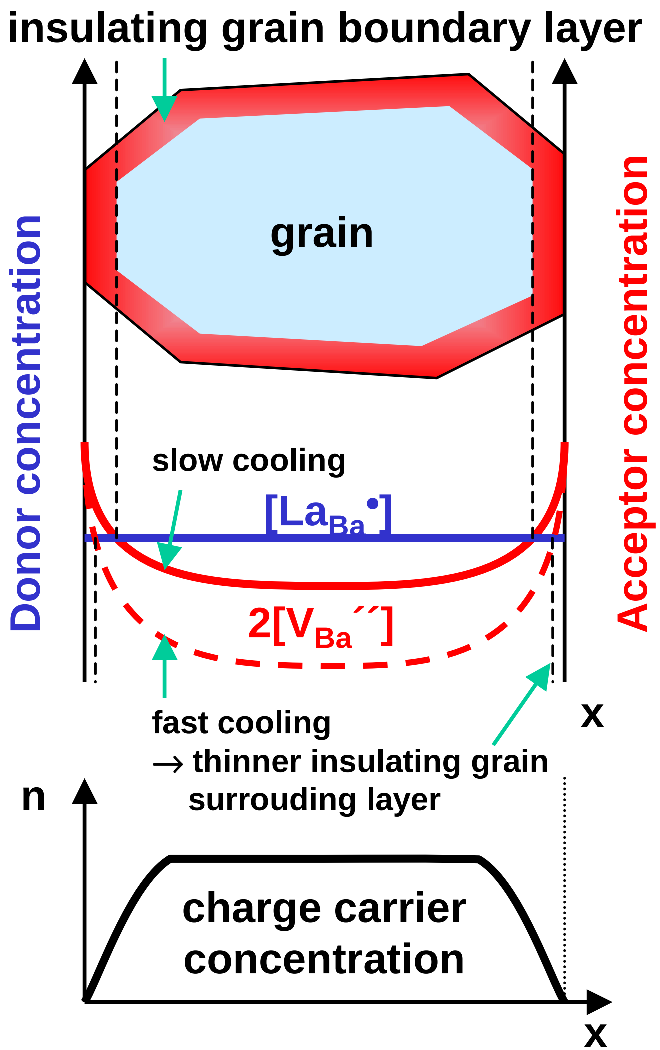
Heater

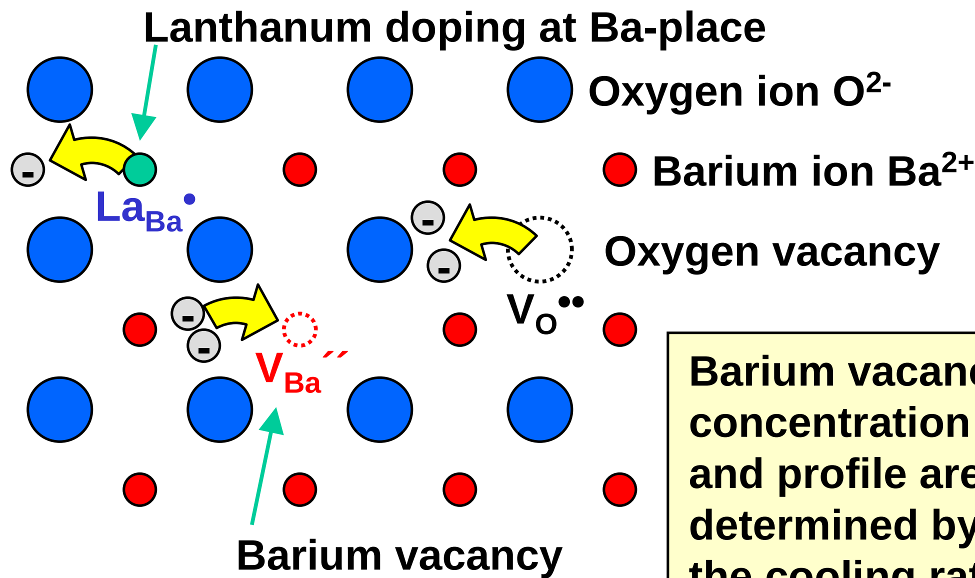
heat emission



- **heating components self-regulating**

Nonlinear Resistors / PTC
Vacancy and Doping Profile

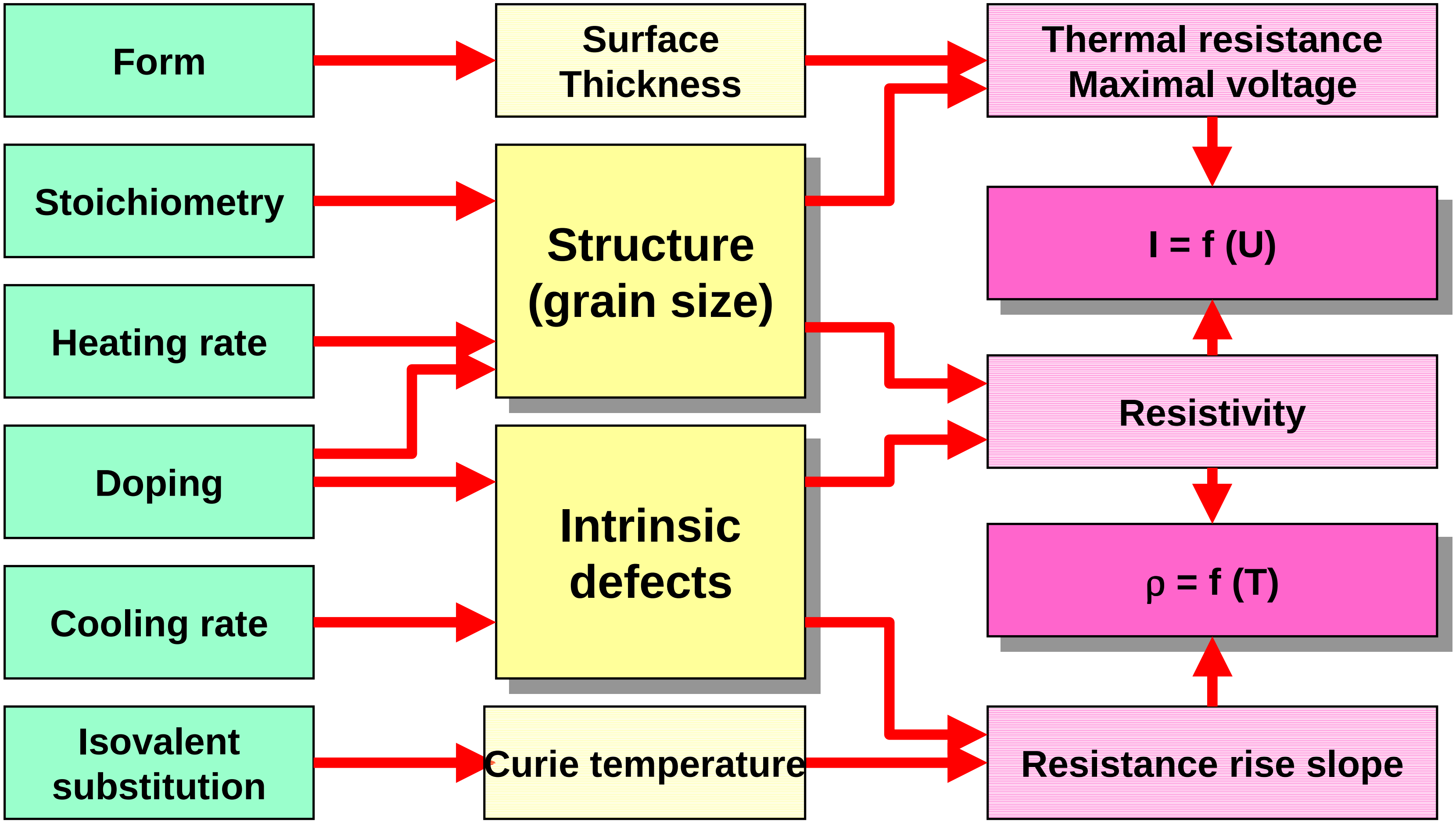




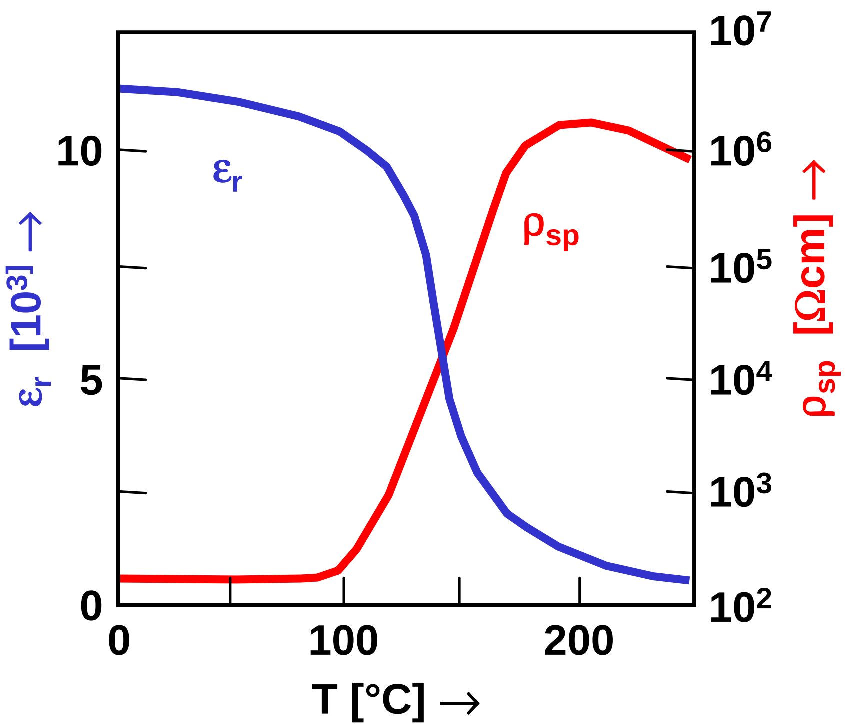
Barium vacancy concentration and profile are determined by the cooling rate

V_{Ba}'':	Ba-vacancy (acceptor)
$V_O^{\bullet\bullet}$:	O-vacancy (donor)
$La_{Ba}^{\bullet}$:	La^{3+} (doping) at Ba^{2+}-place, (donor)
⊖ e´, (n):	electron (-concentration)

Nonlinear Resistors / PTC
Material Engineering with Ceramic PTC Resistors

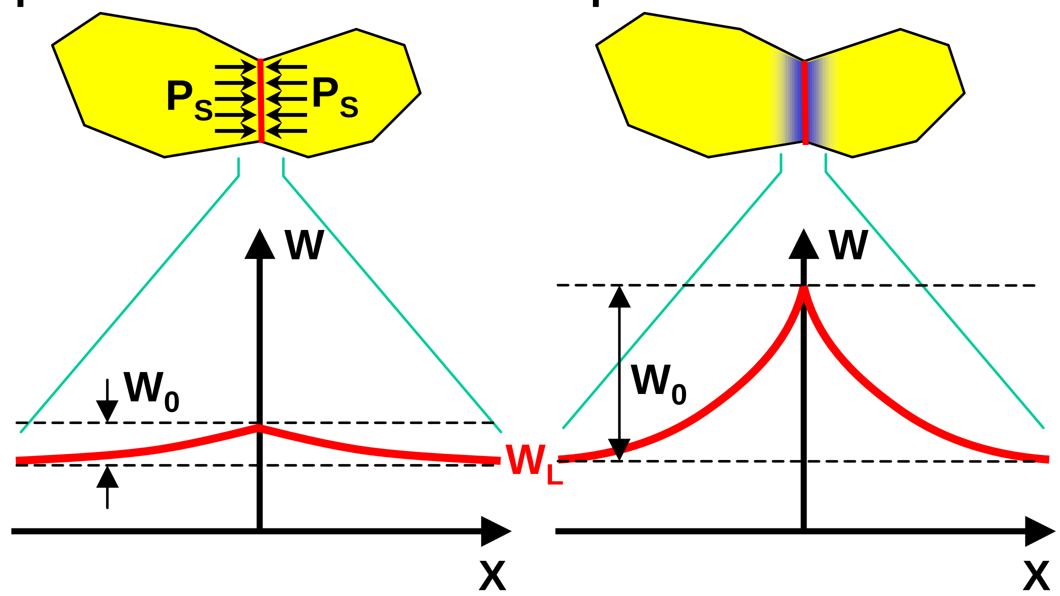


Nonlinear Resistors / PTC
Temperture-dependent Potential Barrier at Grain boundary in $BaTiO_3$



$T < T_C$: ferroelectricity → spontaneous polarization

$T > T_C$: disappearance of the spontaneous polarization



polarization charges compensate negative grain boundary charges → W_0 small

space charges compensate negative grain boundary charges → W_0 large

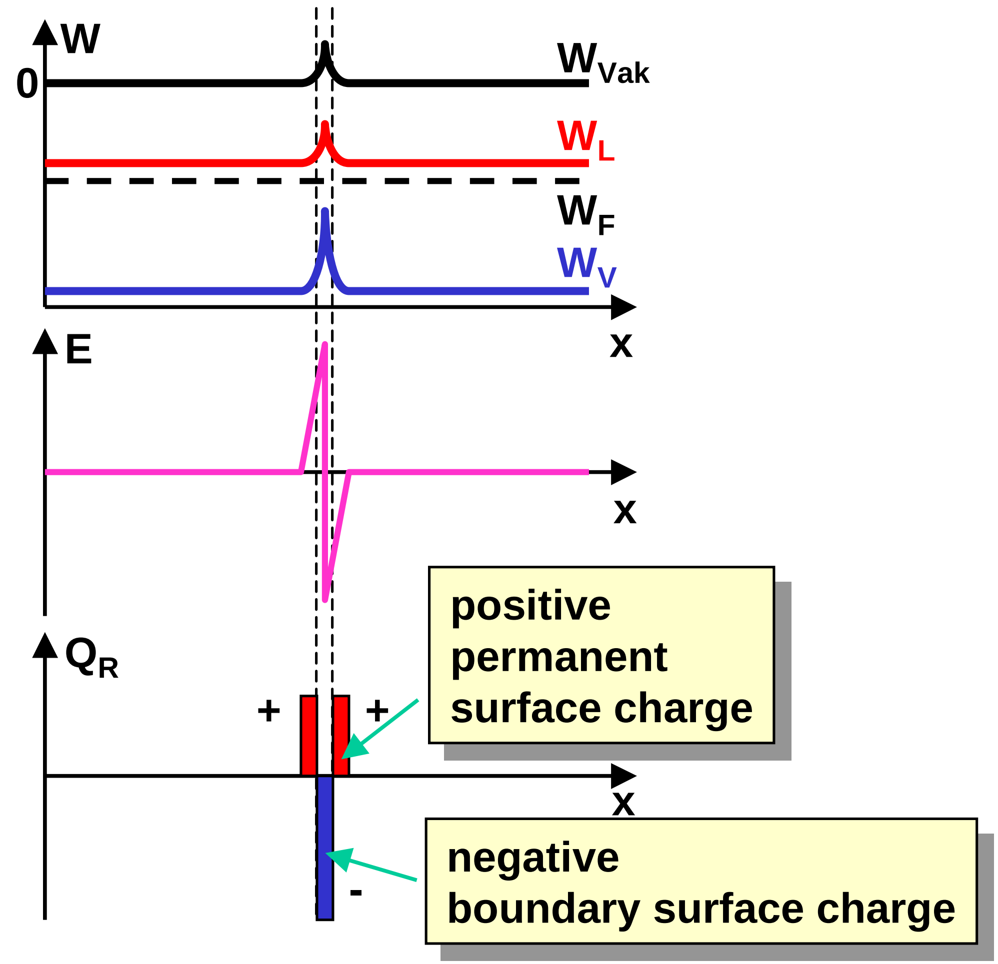
$$W_0 \sim \varepsilon_r^{-1} \sim T - T_C$$

$$\rho_{sp} \sim e^{\frac{W_0}{kT}}$$

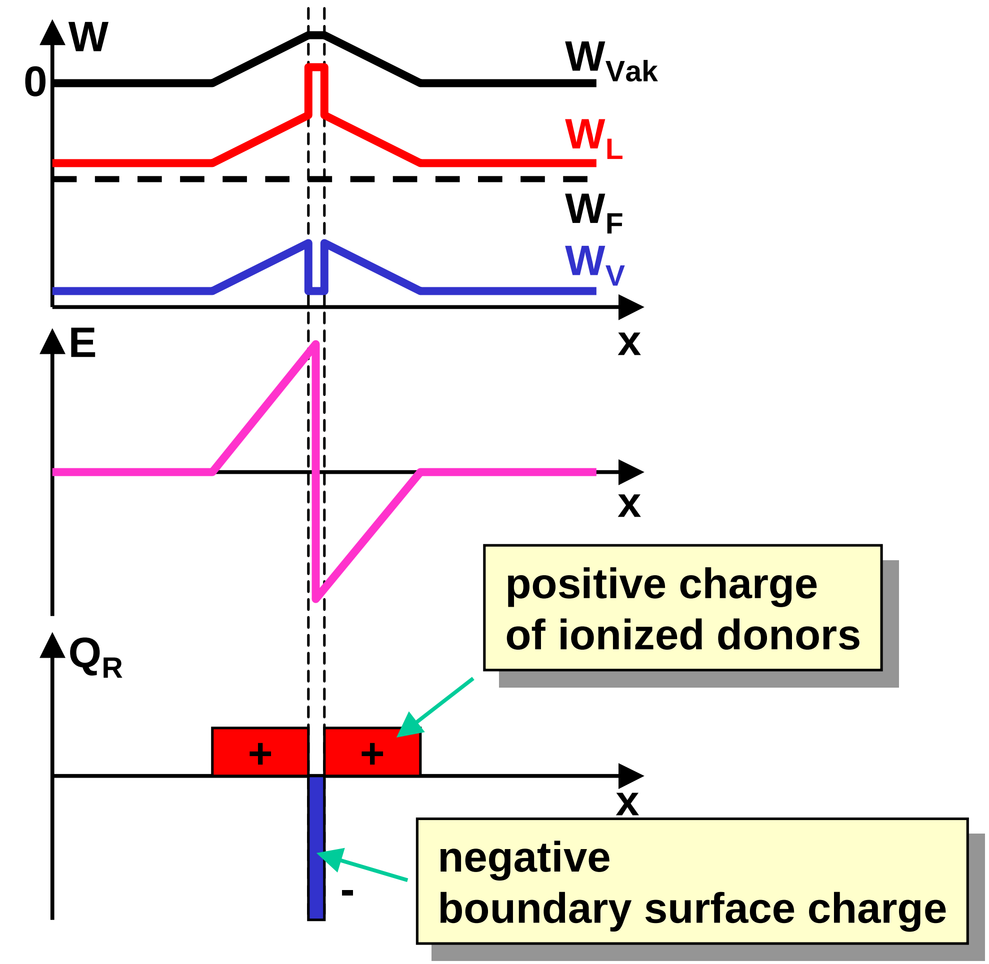
Nonlinear Resistors / PTC

Band Model, E-field Strength and Space Charge at the Grain Boundary

$T < T_C \rightarrow$ ferroelectricity: permanent dipole

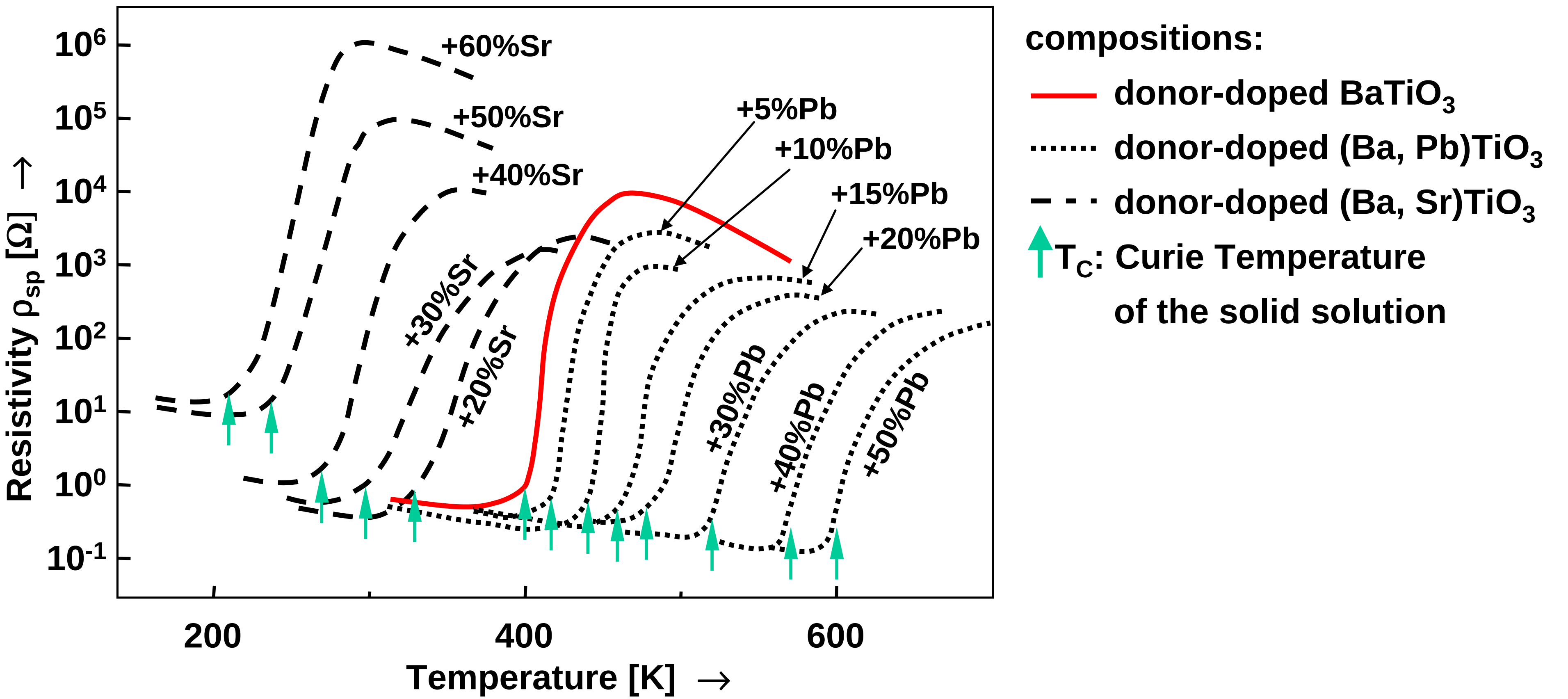


$T > T_C \rightarrow$ space charge of ionized donors



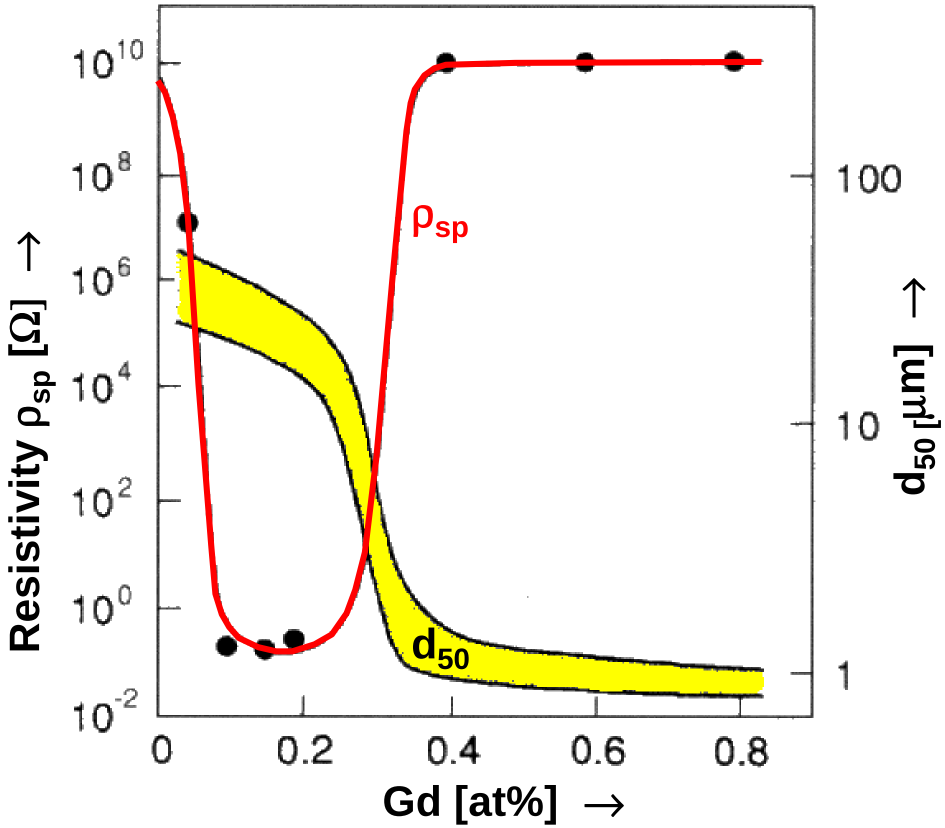
Nonlinear Resistors / PTC

Temperature dependence of resistivity ρ_{sp} of PTC ceramics



Ferroelectric, semiconducting $BaTiO_3$ shows an anomaly of resistance at $T>T_C$ (PTC-effect)

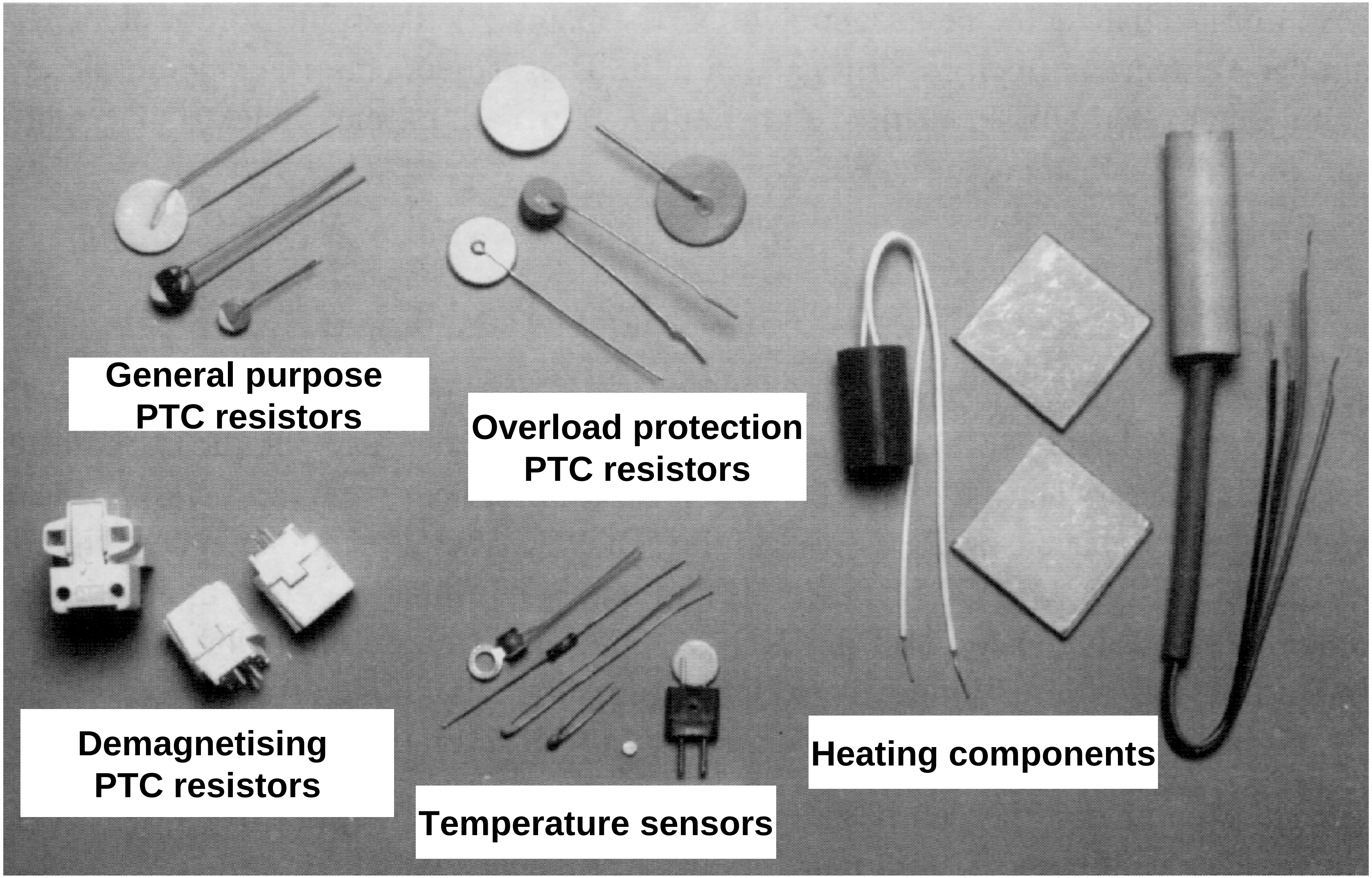
Nonlinear Resistors / PTC
Middle Grain Size and ρ_{sp} as a Funktion of the Dopant Concentration



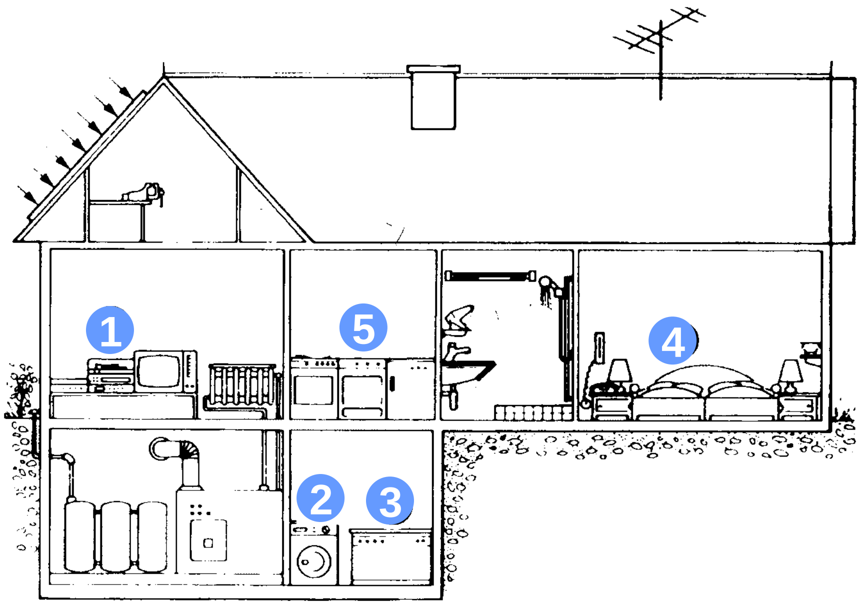
- **donor doping in perovskite**
  $BaTiO_3$ ($A^{2+}B^{4+}O^{2-}_3$)
  - **→ A^{3+} in stead of Ba^{2+}: La^{3+}, Y^{3+}, Gd^{3+}**
  - **→ B^{5+} in stead of Ti^{4+}: Sb^{5+}, Nb^{5+}, Ta^{5+}**
- **doping effects**
  - **→ decrease of the resistivity ρ_{sp} (electron conduction) only with donor concentration ≤ 0,3 at%**
  - **→ decrease of the middle grain size d_{50} with increasing donor concentration**

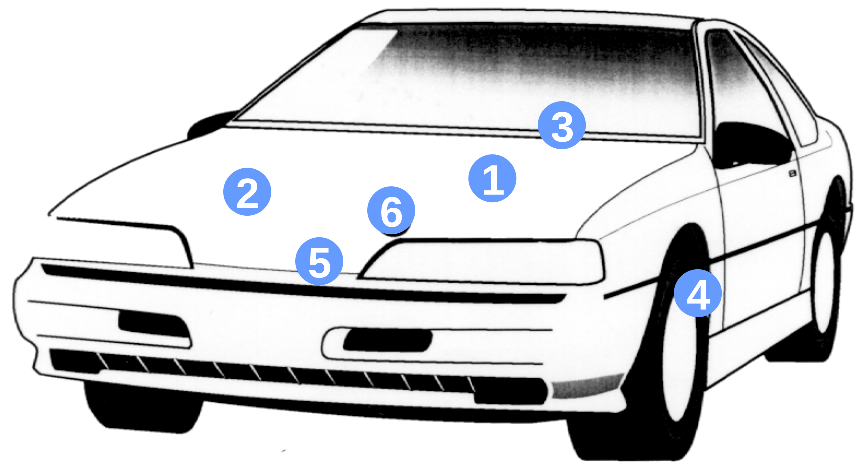
variation of ρ_{sp} und d_{50} :	**independent of the type of donor** **strongly dependent on the donor concentration**

Nonlinear Resistors / PTC
Device Description



Nonlinear Resistors / Varistors
Applications of Varistors

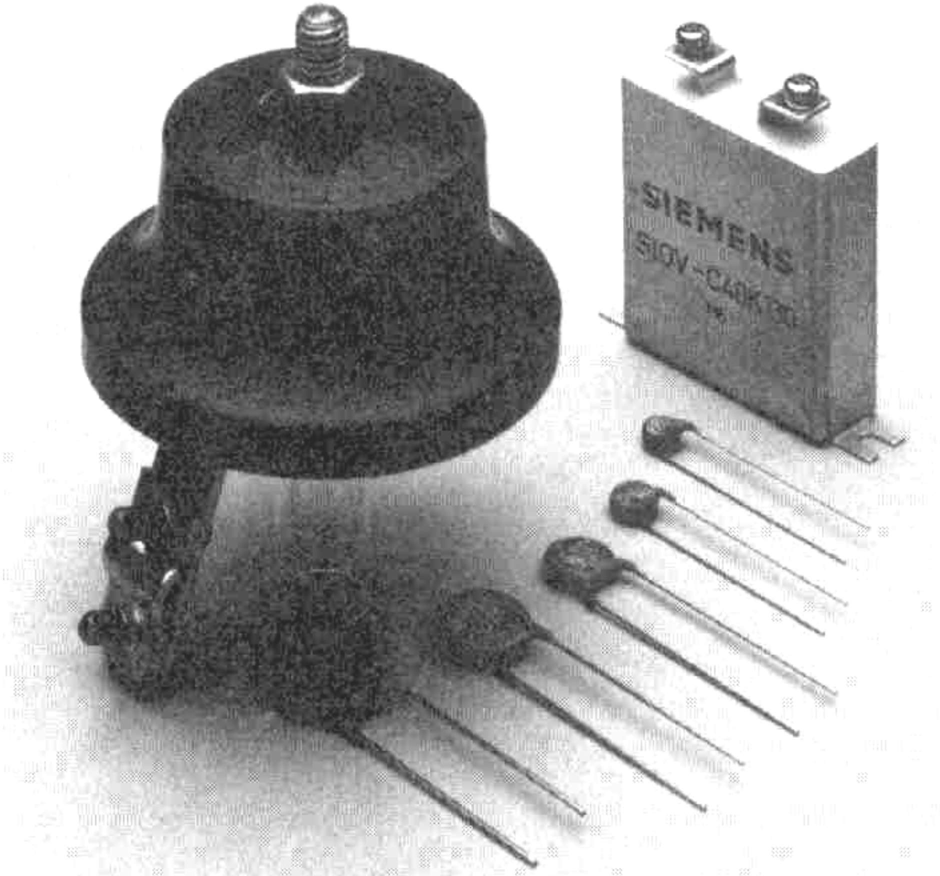


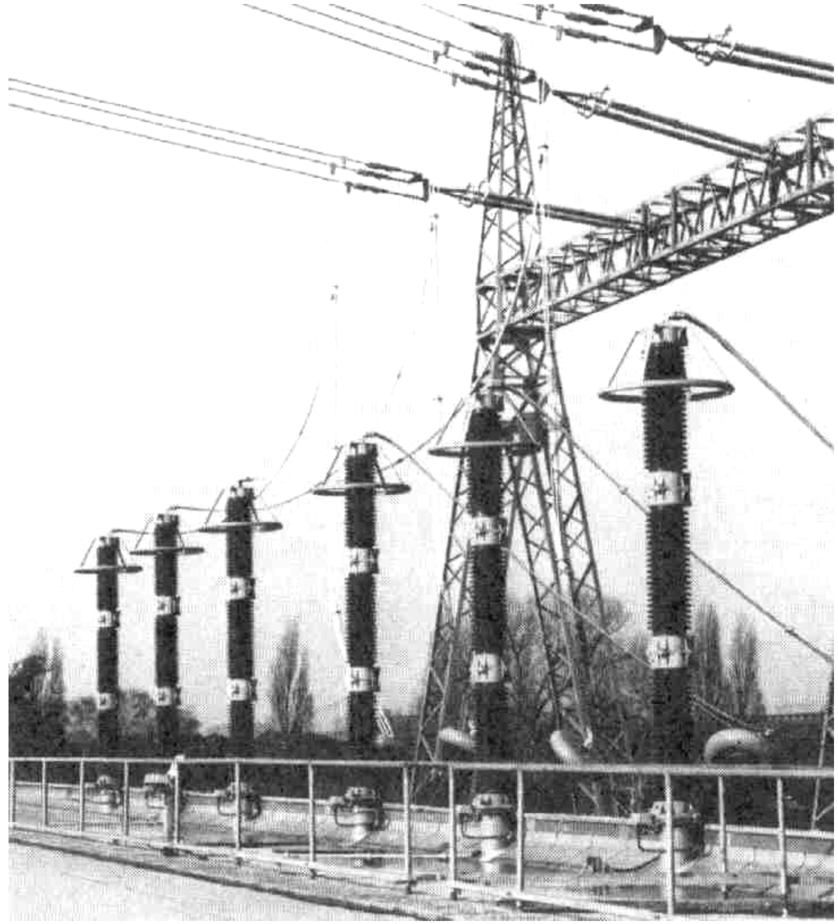


1. Lightning protection for television, video, PC, ...
2. Washing machine
3. Deep-freezer
4. Telephone
5. Total protection

1. Central electrical system protection
2. Overvoltage-protected electronic ignition
3. Airbag
4. ABS
5. Board computer
6. Combination protection

Nonlinear Resistors / Varistors
Examples

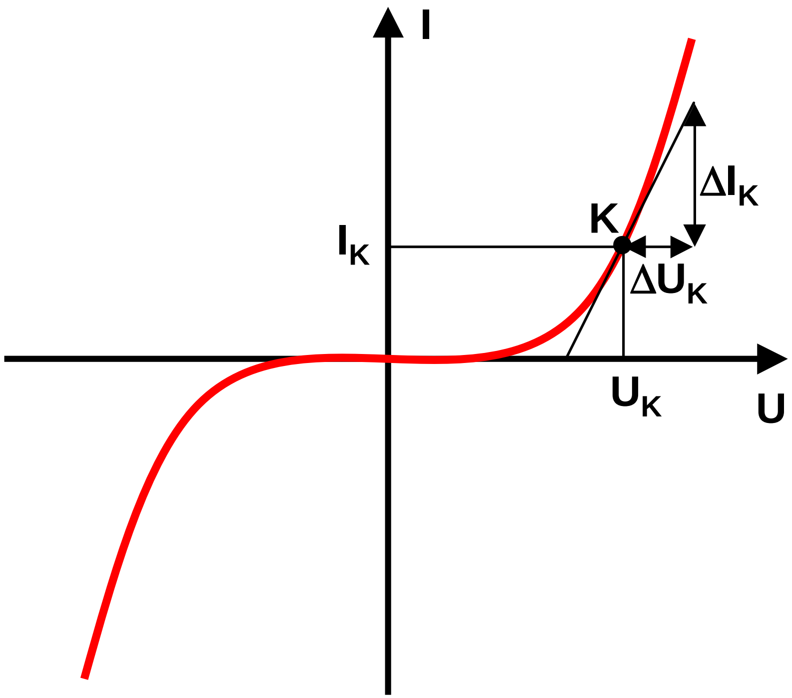




• **Designs of ZnO Varistors**

• **Varistors as high voltage deflector**

Nonlinear Resistors / Varistors
Current-Voltage-Characteristic Curve



Varistor

Variable Resistor

voltage-dependent resistance
with symmetric I(U)-characteristic curve

$$I = \pm K \cdot |U|^{\alpha}$$

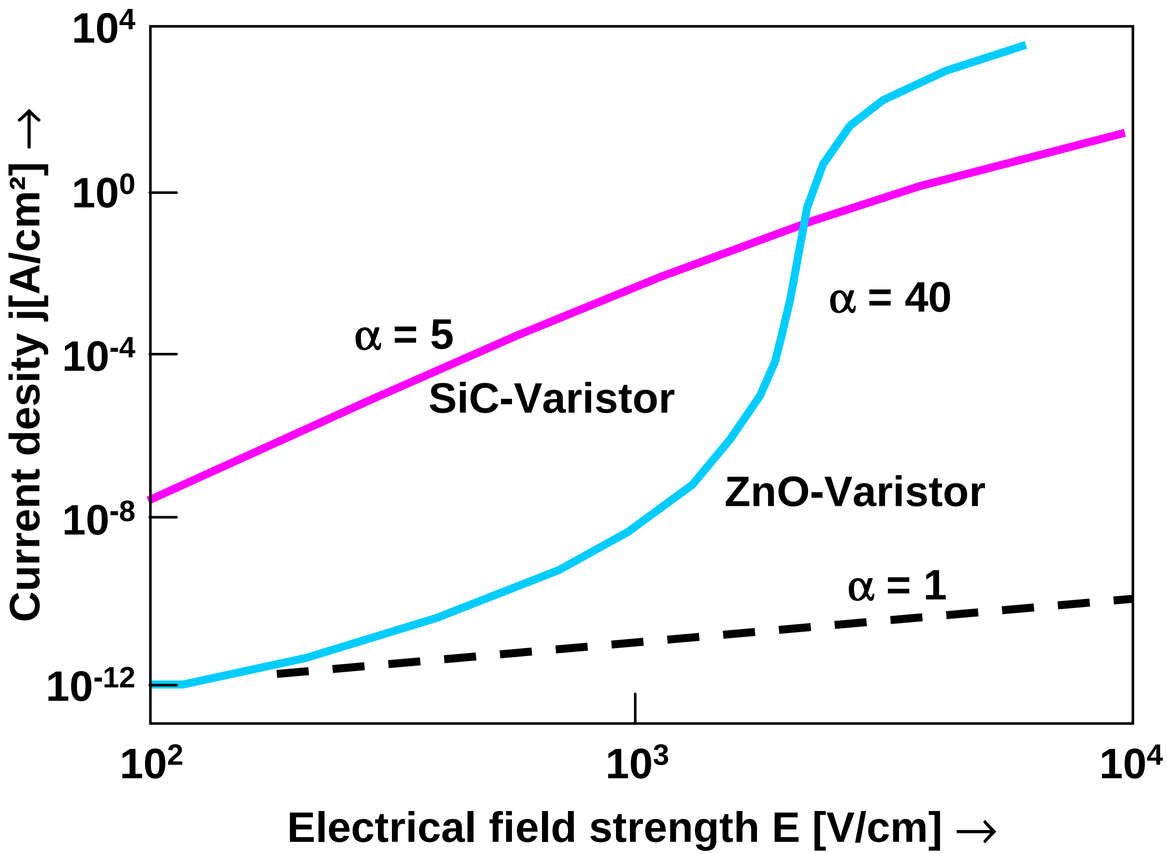
geometry-dependent constant K

nonlinear coefficient α

typical α-values: 5...70
Materials: SiC, ZnO

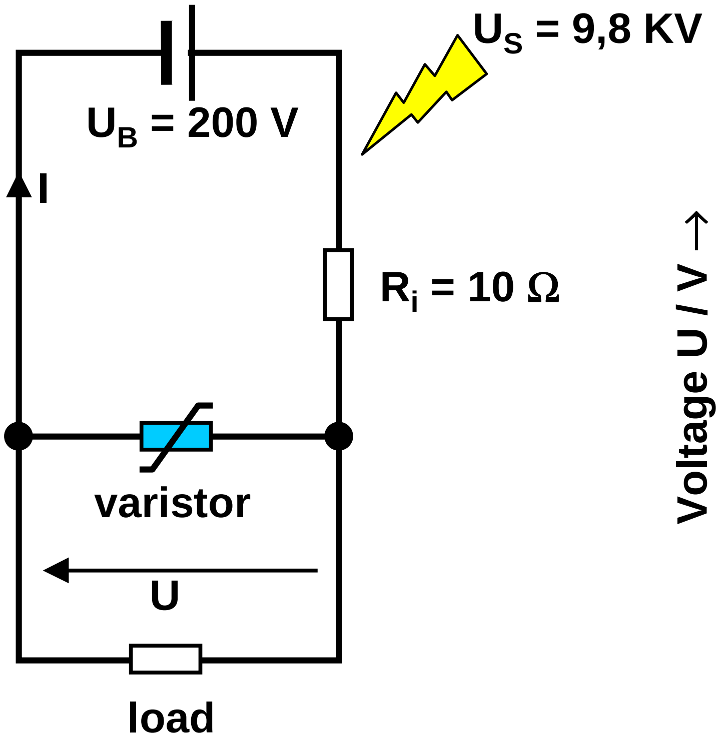
application of varistors as protection from overvoltages

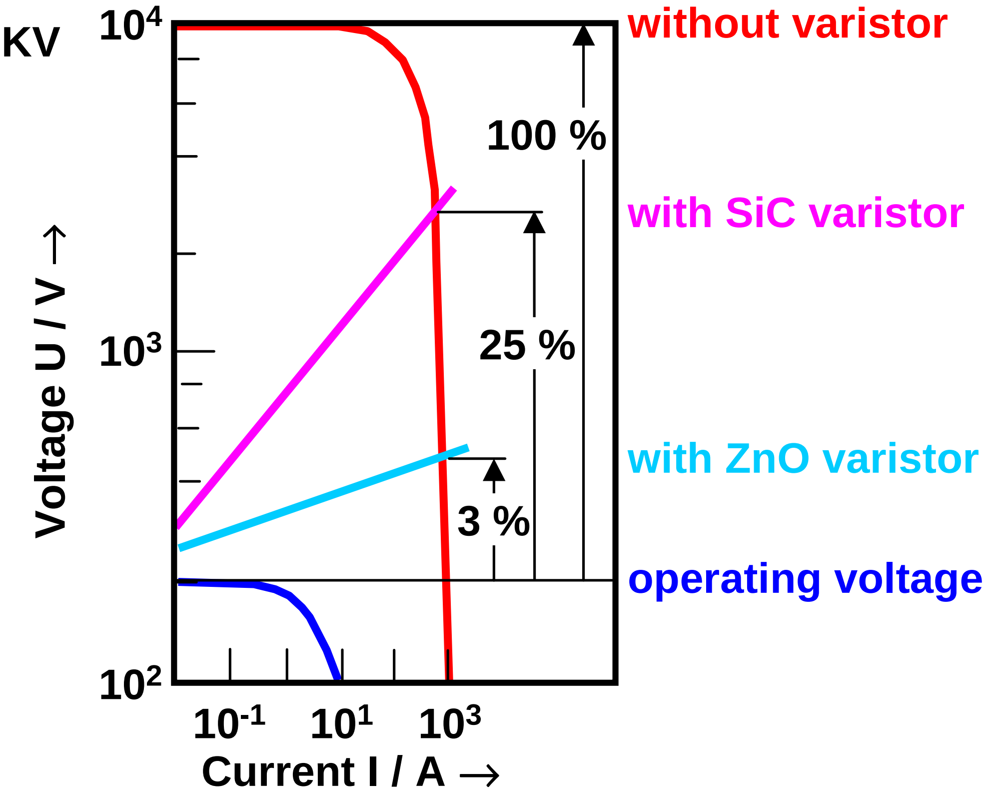
Nonlinear Resistors / Varistors
Current-Voltage-Curve of SiC and ZnO Varistors



- **ohmic resistance α = 1**
- **silicon carbide SiC varistor**
  p-type (Al-doped) SiC
  grain size approx. 100 µm
  α ≈ 5...7
- **zinc oxide ZnO varistor**
  n-type doped ZnO with
  insulating grain boundaries
  grain size variable:
  < 1 µm to 100 µm
  α-values from 30...70
  very low leakage current

Nonlinear Resistors / Varistors
Comparison of SiC and ZnO Varistors as Overvoltage Protection





The voltage U is temporary increased by an interference voltage $U_S(t)$.

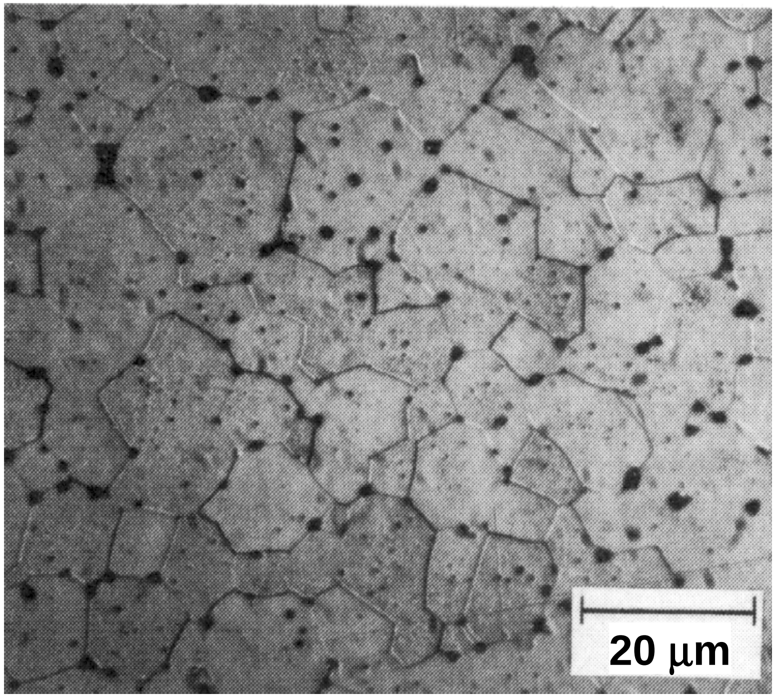
$$U(t) = U_S(t) + U_B - R_i \cdot I(t)$$

Double-logarithmic curve U(I)

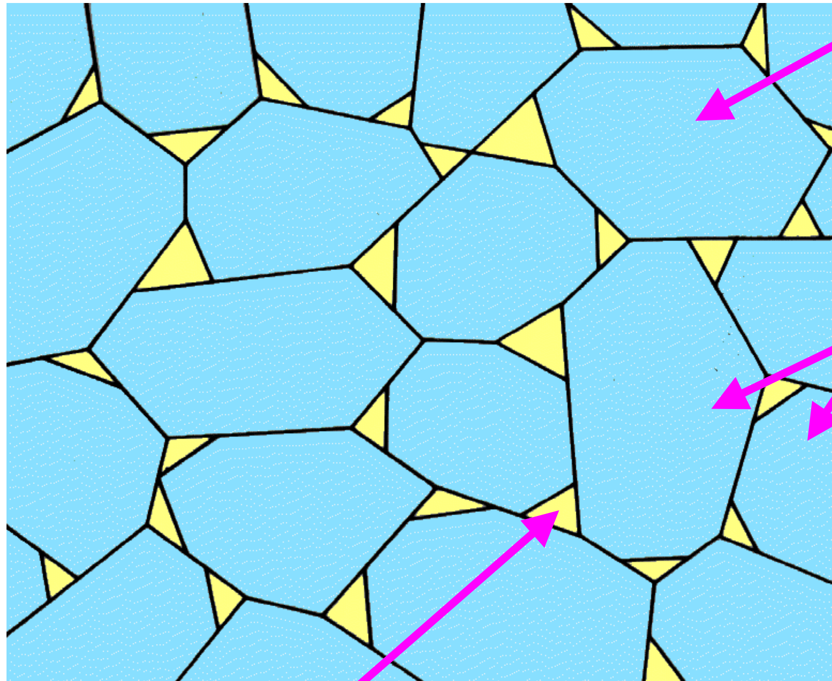
- **during normal operating voltage**
- **during overvoltage U_S = 9,8 kV**

Nonlinear Resistors / Varistors
Polycrystalline ZnO - Structure with Secondary Phases

Micrograph of a ZnO varistor ceramic



Scheme of the structure of a ZnO varistor ceramic



ZnO grain size variable by doping/ sintering process

A pair of grains "micro- varistor"

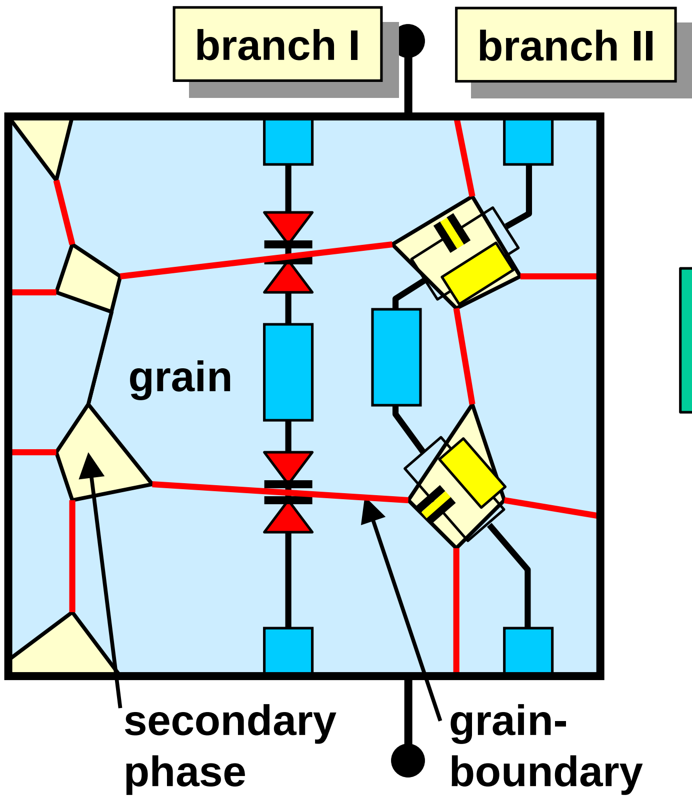
Gusset, from dopants with the sintering process, the "secondary phases" are formed.

Polycrystalline ceramic:	**network from parallelly and serially connected micro-varistors**
Varistor operating voltage:	**depending on the grain size and geometry of the component**

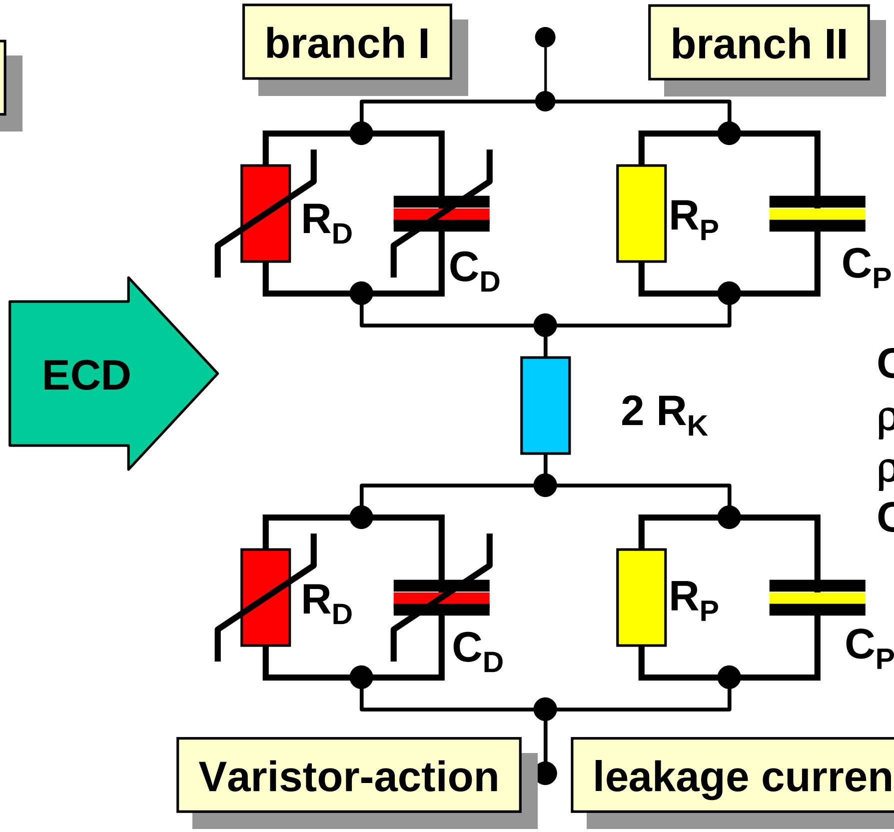
Nonlinear Resistors / Varistors

Polycrystalline ZnO - Structure: Eq. Circuit Diagram for Micro-varistors

- **structure scheme**



- **equivalent circuit diagram**



$C_D \cong 240$ nF/cm²
$\rho_K \cong 1$ Ωcm
$\rho_P \cong 80$ kΩcm
$C_P \cong 90$ nF/cm²

Series connection of grain resistance (R_K) and barrier layer resistance (R_D) parallel connection of R_D and C_D R_D and C_D: voltage-dependent

leakage current action regions R_P, C_P parallel to the varistor-action grain boundaries

Nonlinear Resistors / Varistors
Polycrystalline ZnO - Ceramic: Summary

- **Varistor effect in doped ZnO ceramic is a characteristic of the grain boundary region.**

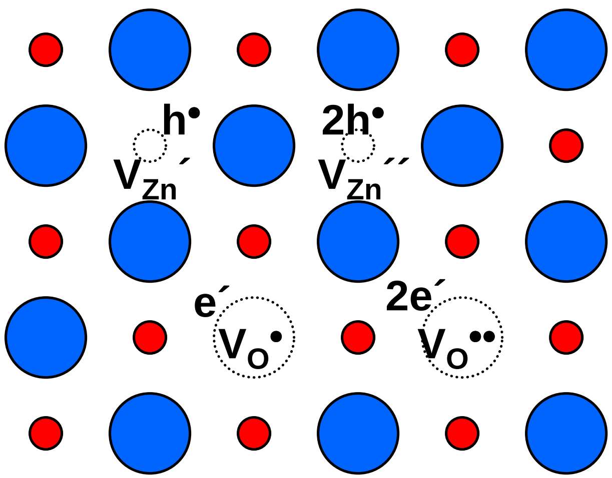
  ZnO grains are low impedance.
- **Varistor effect occurs at pairs of grains, which in direct contact to each other.**
- **Varistor effect starts with a breakthrough voltage of approx. 3,0 ± 0.5 V / grain boundary.**
- **Grain boundary region forms a potential barrier of 0,6 eV.**
- **Response time of the nonlinear current is within several nanoseconds**
- **Available varistor system: ZnO + Bi_2O_3 + MnO_2 + Co_3O_4 + Sb_2O_3 + Cr_2O_3 + further additives**

  (up to 10 components are common practice, reason: optimization of the secondary characteristics of the respective type of varistor).

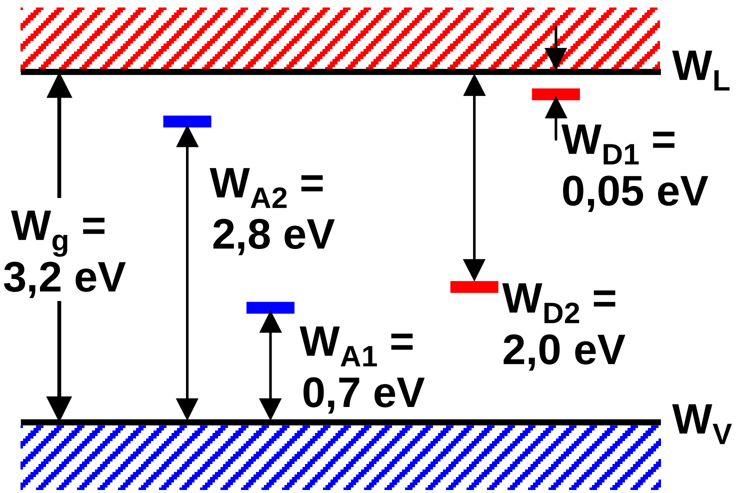
Schottky-Defects and Band Scheme in ZnO

Schottky-defects in ZnO

(2-dimension illustration)



$n + [V_{Zn}´] + 2[V_{Zn}´´] = p + [V_O^{•}] + 2[V_O^{••}]$



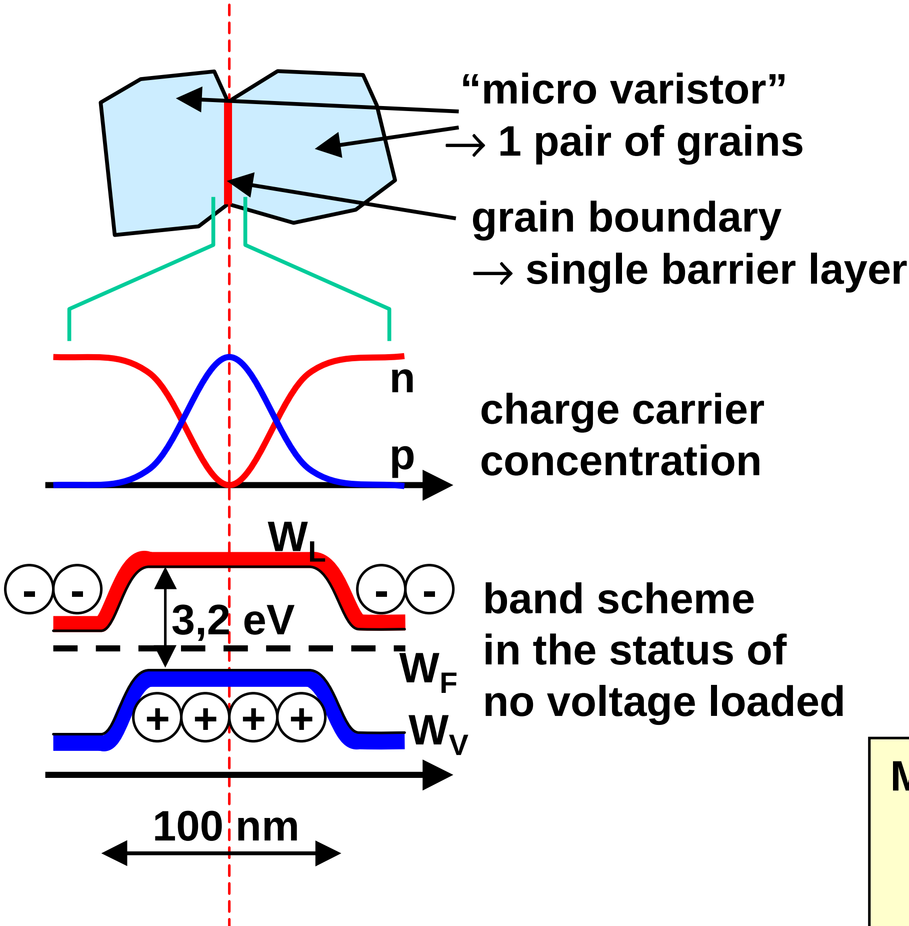
Band scheme with the energy levels of the Schottky-defects (W_A, W_D)

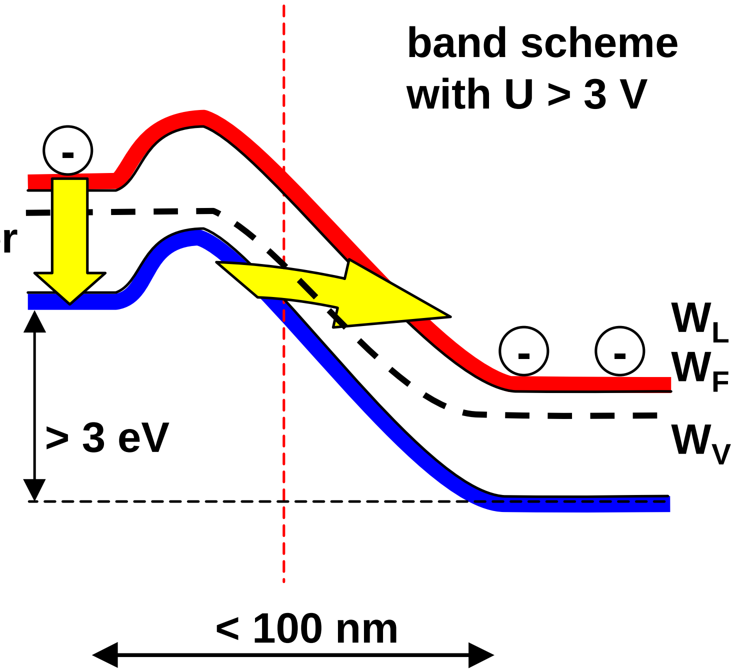
$V_{Zn}´$, $V_{Zn}´´$:	one or two charged Zn-vacancy
$h^{•}$, (p):	defect elektrons (concentration)
$V_O^{•}$, $V_O^{••}$:	one or two charged O-vacancy
e´, (n):	electrons (concentration)

(W_{A1}, W_{A2}) A: acceptors

(W_{D1}, W_{D2}) D: donors

Nonlinear Resistors / Varistors
Band Model of ZnO Varistor at Grain Boundary





Model conception:
Band-Band-Tunneling of electrons though a high impedance track region to both side of the grain boundary

Nonlinear Resistors / Varistors

Adjustment of the High Impedance Track Region at the Grain Boundary

- **Production (sintering temperature ≈ 1300 °C)**

  ⇒ high-temperature equilibrium:

  excess of oxygen vacancy

  charge carrier: $n = [V_O^{\bullet}] + 2 \cdot [V_O^{\bullet\bullet}]$

- **Operating temperature < 100 °C**

  ⇒ low-temperature equilibrium:

  $[V_{Zn}'] + 2[V_{Zn}''] \approx [V_O^{\bullet}] + 2[V_O^{\bullet\bullet}]$

  ⇒ n very small