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Noise-based techniques for gas sensing

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Outline

- Introduction to noise and fluctuation-enhanced sensing (FES)
- Adsorption-desorption noise in gas sensors
    - Frequency and time domain response
- 1/f noise in gas sensors
- Higher order statistics
- Precautions
- Conclusions

Introduction-general

- Electronic nose:
  - arrays of N detectors with different selectivity for detection of M species (N>>M)
  - Pattern recognition algorithms for selectivity
- Noise is considered as detrimental in sensing as it reduces the S/N ratio
- But noise is also a signal [Bruschi& *Sensors and Actuators B*, **19** (1994) 421]
- Fluctuation enhanced sensing (FES): [Kish&, *Sensors and Actuators B*, **71**(2000)55]
  - employ patterns in noise characteristics of microfluctuations (e.g. spectra)
  - →reduction of number of sensing elements
  - In theory: one sensor could resolve mixture of gases

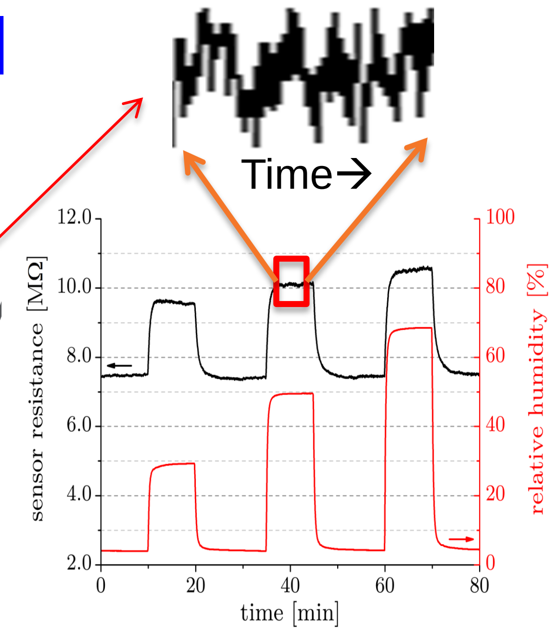


fig. from [Steinhauer et al. APL2014]

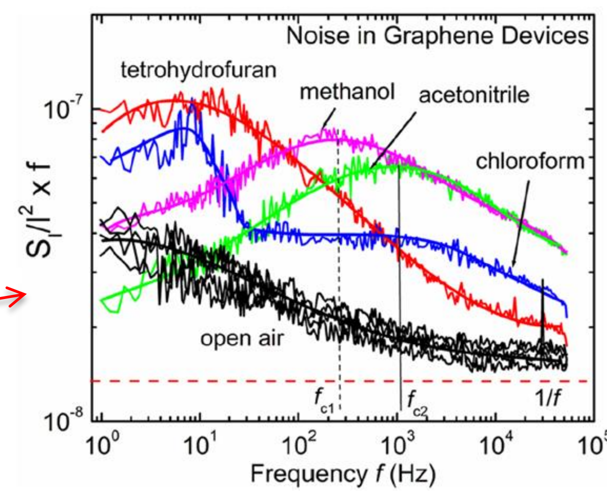
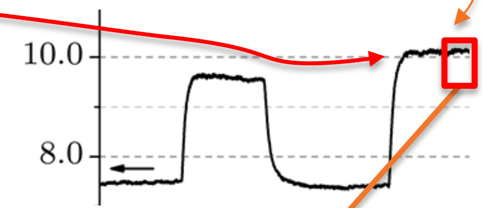


fig from [Rumyantsev, Nanolett. 12 (2012) 2294]

Noise basics

- We are interested in stationary fluctuations!!!: I(t), U(t), R(t), G(t)…



Mean value

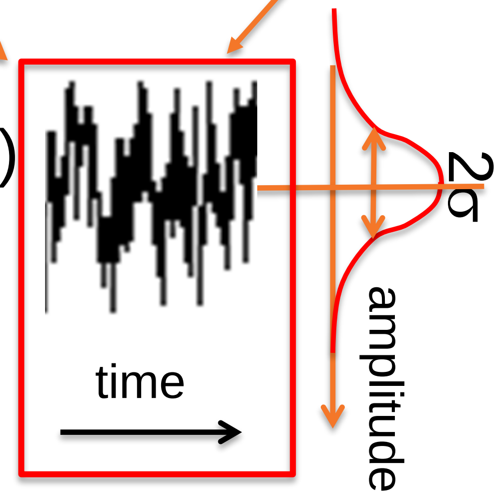
$$I_{TOTAL}(t) = \langle I \rangle + I(t)$$

Stochastic component

I(t) $\xrightarrow{\text{FFT}}$ $$Y(\omega) = \int I(t)\exp(-i\omega t)dt$$

$$S_I(\omega) = \lim_{T\to\infty} \int \frac{2|Y(\omega)|^2 d\omega}{T}$$ Power spectral density (PSD) of current fluctuations

$$\sigma^2 = \text{var} = \left\langle \left(I(t) - I_{mean}\right)^2 \right\rangle = \int S_I(f)df$$



PSD is FFT of autocorrelation function $c(\tau) = \langle I(t)I(t+\tau) \rangle$

$$S_I(\omega) = 4\int c(\tau)\cos(\omega\tau)d\tau$$

→different time domain waveforms can give the same PSD → information lost

Noise in (chemi-)resistors

$$I(t) \approx qN(t)\mu(t)E$$

$$S_I(\omega) \propto (dI)^2$$

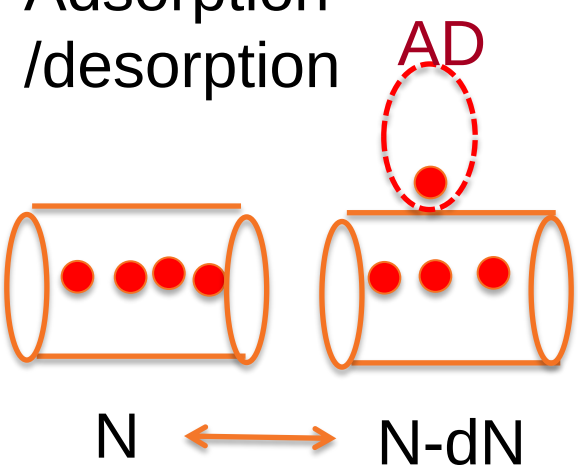
$$dI \approx \mu dN + N d\mu$$

$$\frac{S_I}{I^2} = \frac{S_U}{U^2} = \frac{S_R}{R^2} = \frac{S_G}{G^2}$$

Carrier number fluctuations

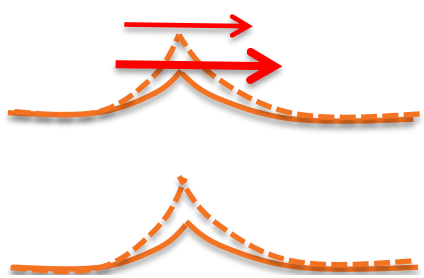
Mobility fluctuations

Adsorption /desorption



[Gomri&, J.Phys. D.Appl. Phys41(2008)065501]

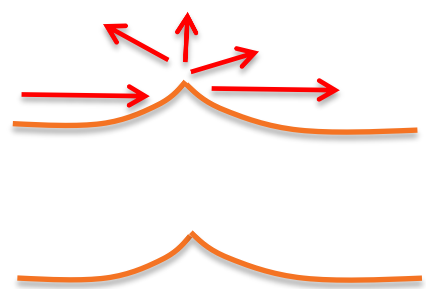
Barrier height fluctuations at grain boundaries



Surface diffusion too

[Schmera&, I3E Sens J.10(2010)461]

Scattering on defects (charged, surface roughness,...)

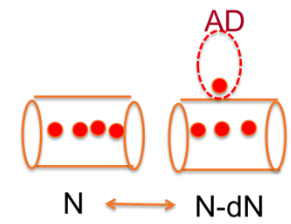


[Hooge, I3E TED, 41(1994)1926]

Adsorption / desorption (A/D) noise

[In semiconductors known as generation-recombination and random telegraph signal (RTS) noise (defect occupancy fluctuations)]

dN=1



$$\tau = \frac{1}{(1/\tau_{ad} + 1/\tau_{des})}$$

$$S_I(f) = \frac{\tau^2}{(\tau_{ad} + \tau_{des})} \frac{4(\Delta I)^2}{1 + [2\pi f \tau]^2}$$

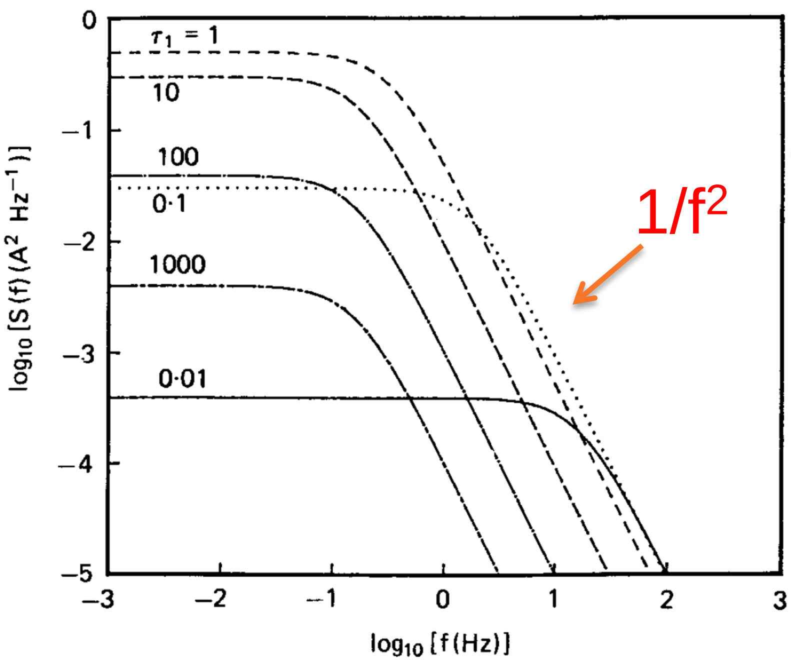
[Machlup, JAP, 25(1954)341]

adsorption

desorption

Single A/D events (one site)

Lorentzian

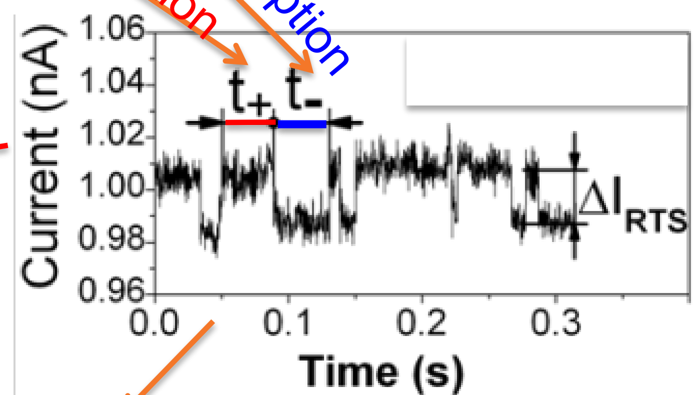


Lorentzian power spectra calculated using equation (2.19 *a*). $\Delta I = 1$ A, $\tau_0 = 1{\cdot}0$ s, $\tau_1 = 0{\cdot}01$–1000 s.

Fig. from [Kirton&Uren, Adv. Phys.1989]

1/f²

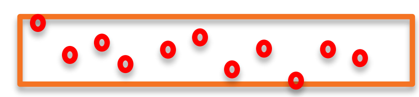
spectrum



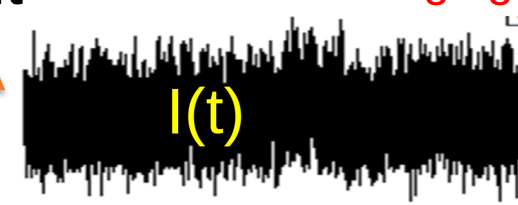
$\tau_{ad} = t_+$

$\tau_{des} = t_-$

Ensemble of sites with the same A/D time constant τ_0



Ensemble averaging



spectrum

Adsorption / desorption (A/D) noise

Number of active sites

$$S_I(f) \propto \frac{\tau^2}{(\tau_{ad}+\tau_{des})} \frac{N_{sites}}{1+[2\pi f\tau]^2} \qquad \tau = \frac{1}{(1/\tau_{ad}+1/\tau_{des})}$$

Lorentzian

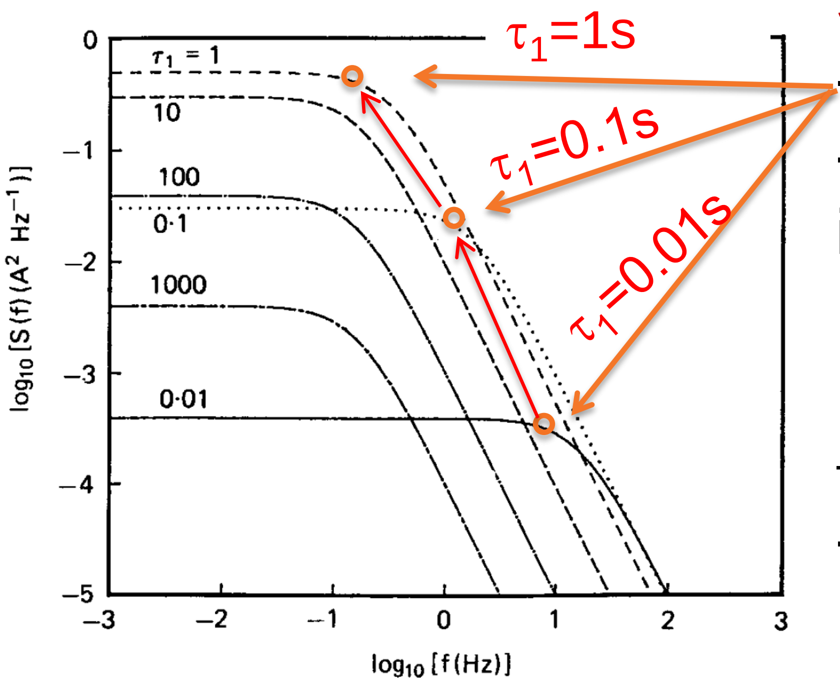
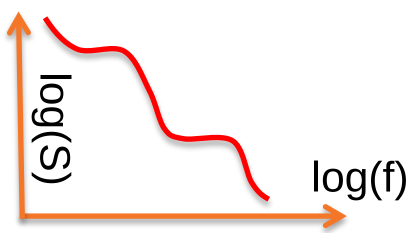


Fig from [Kirton&Uren, Adv. Phys.1989]

Spectral features:

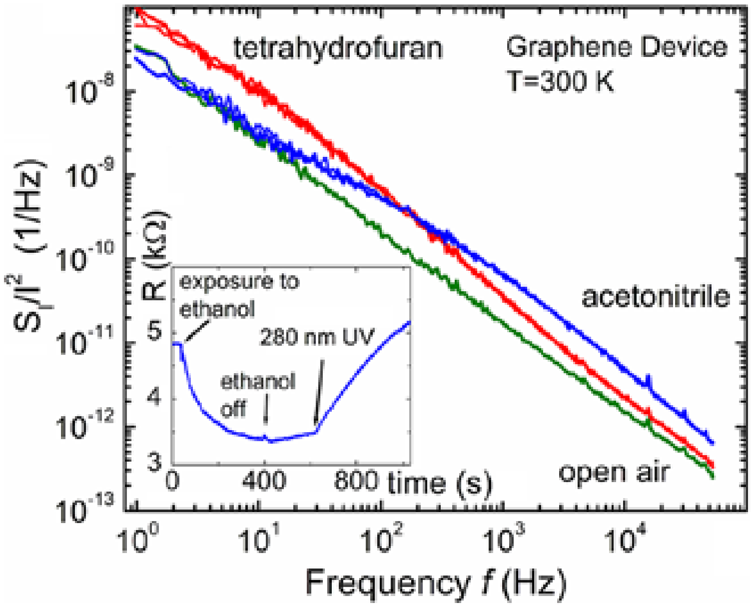
- corner frequency: $f_{cor}=1/(2\pi\tau)$
- →multiple Lorenzians in a mixture of gases



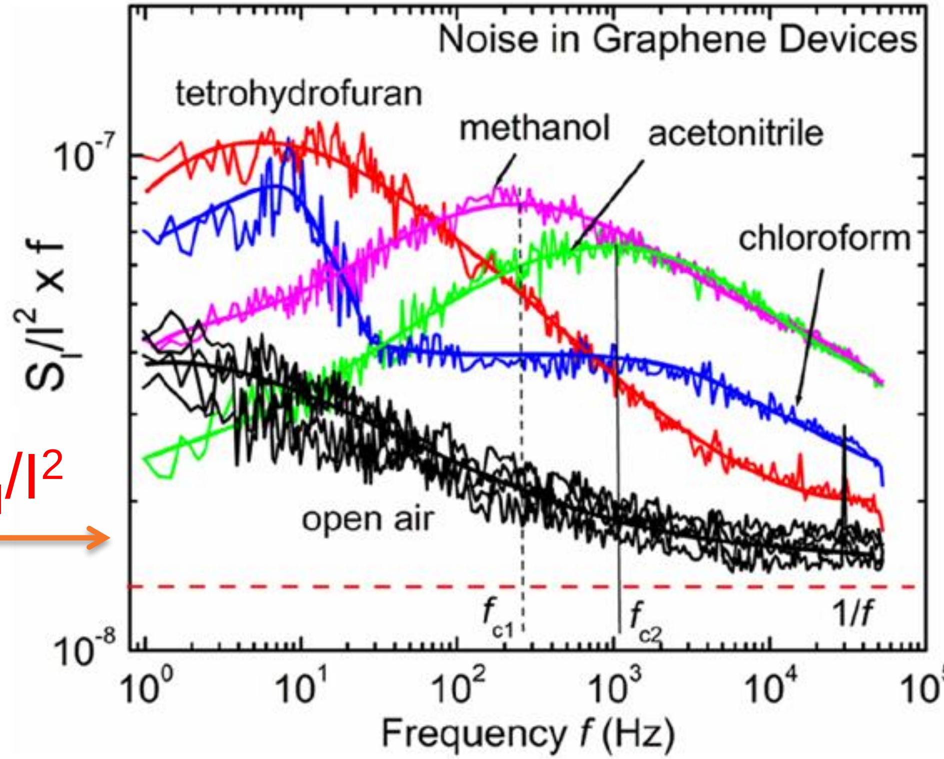
– $\tau_{ad}=f_{ad}(T, p_i,\ldots)$ $\tau_{des}=f_{des}(T, p_i,\ldots)$
- f_{cor} depends on temperature T and partial pressures p_i
- maximum amplitude of PSD occurs for $\tau_{ad}=\tau_{des}$ →proper choise of T, p_i

Graphene sensor

Lorentzian superimposed on 1/f

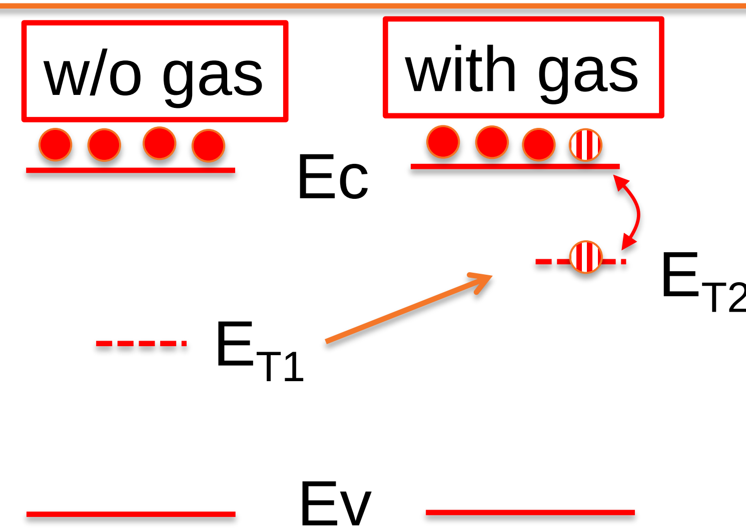


$f.S_I/I^2$



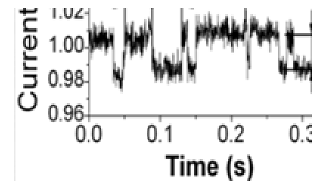
- Reproducible f_{cor} for different gases
- but the A/D time constants from the R(t) measurements are much higher (≈min) that that corresponding to f_{cor} (1-100 ms)
- gas covering can induce g-r noise (modification of existing surface states)

[Rumyantsev, Nanolett. 12 (2012) 2294]

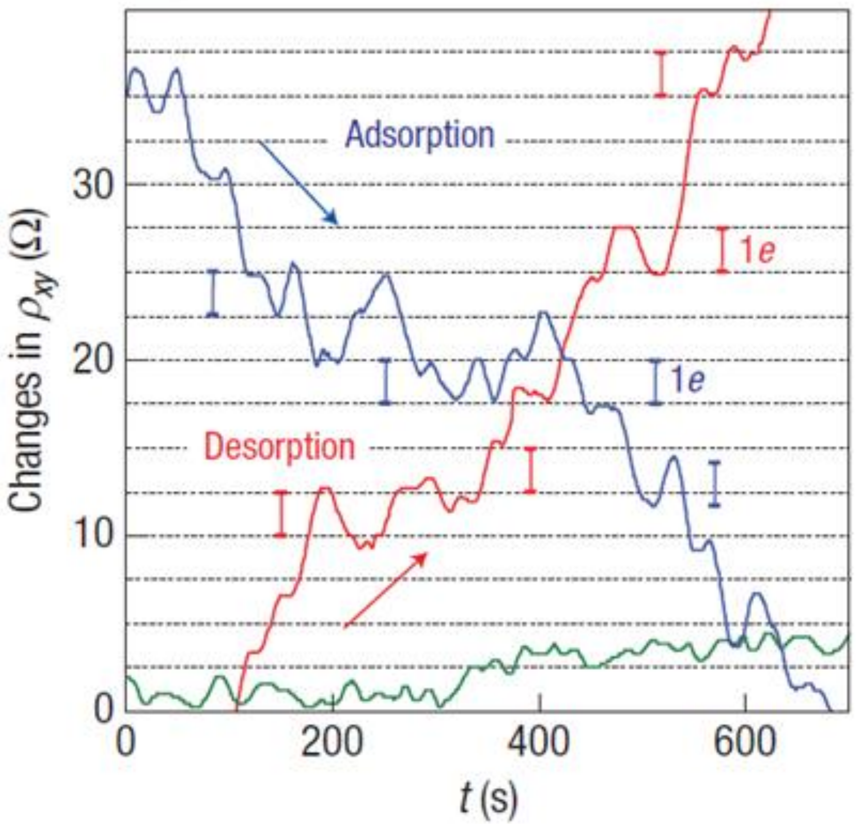


MoS_2,...toooo

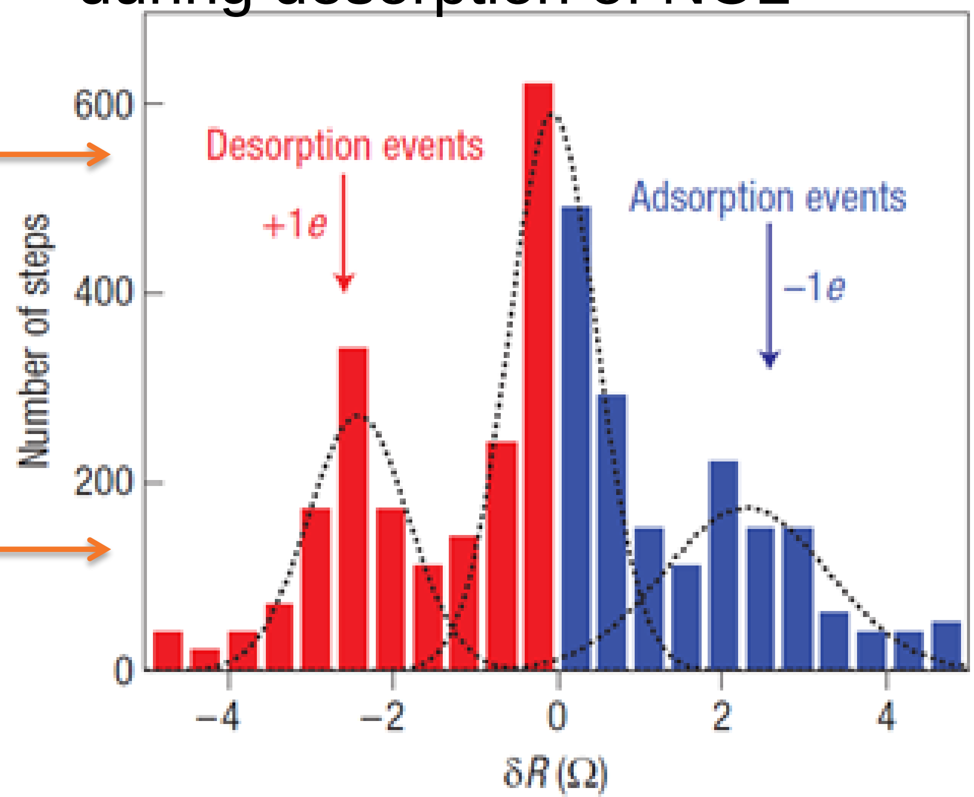
Single adsorption/desorption events in graphene

- Exposure to low concentration of NO2
- Non-equilibrium situation (if equilibium→RTS→ )

Discrete steps: A/D of individual molecules



Histogram of resistance steps during desorption of NO2



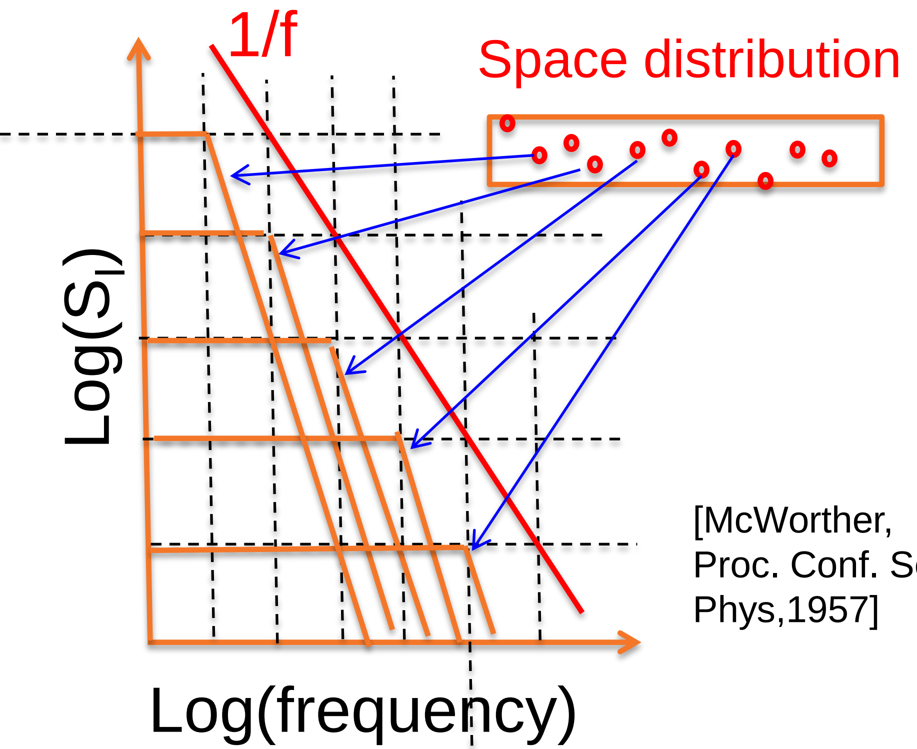
from [Shedin&, Nature, 6(2007)652]

LOGY

Quantized change in R(t)→A/D

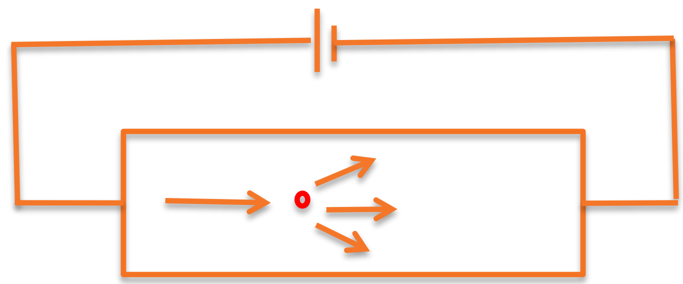
1/f noise

Superposition of simple processes with Lorentzian spectra having a broad distribution of time constants: e.g. carrier number fluctuations



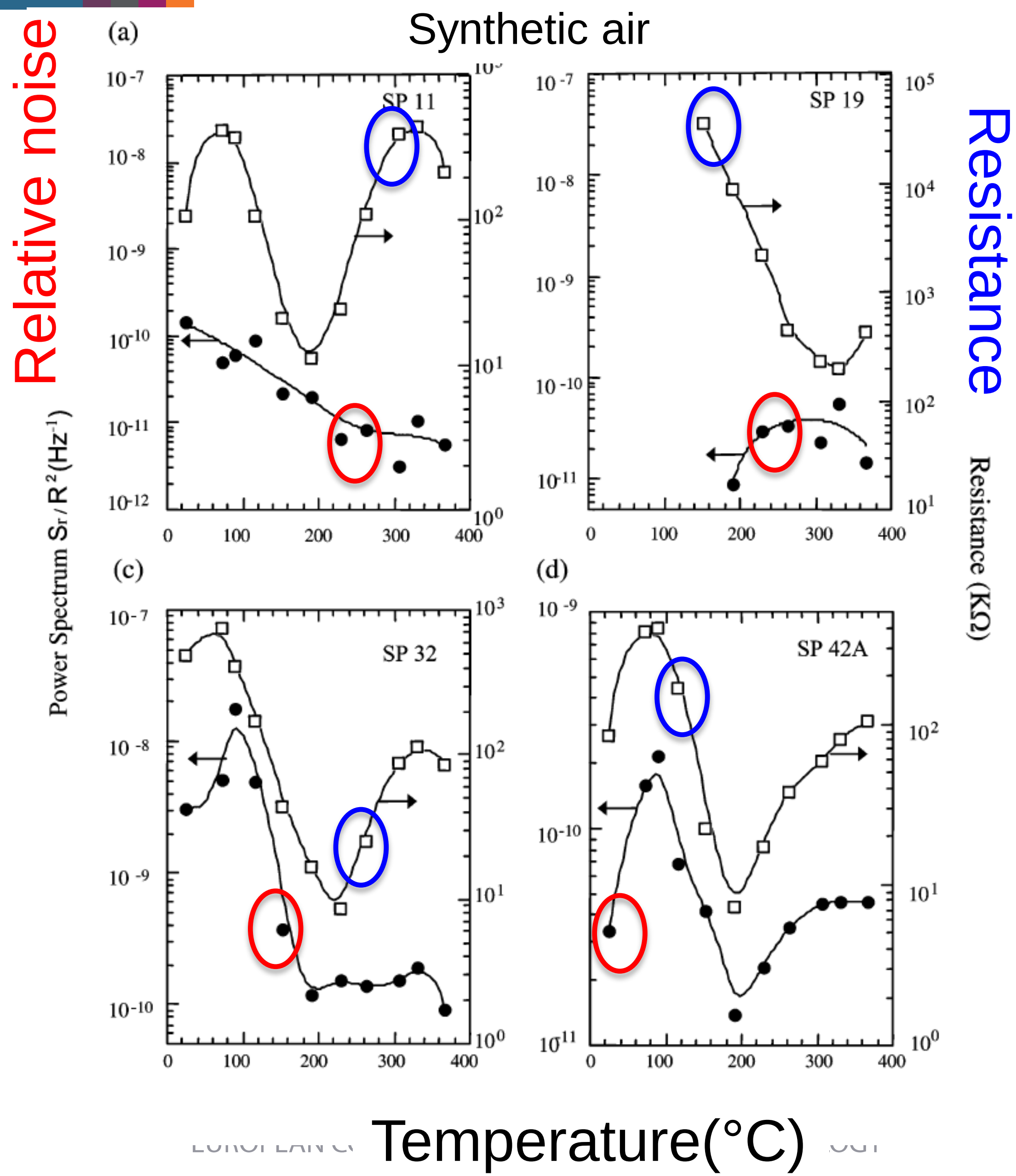
[McWorther, Proc. Conf. Ser Phys,1957]

Complex scattering processes on defects and phonons: even a single scattering center can produce broadly distributed time constants



[Vandamme, Hooge I3E, TED 55(2008)3070]

1/f noise in gas sensor: correlation $S_R/R^2(T)$ vs.



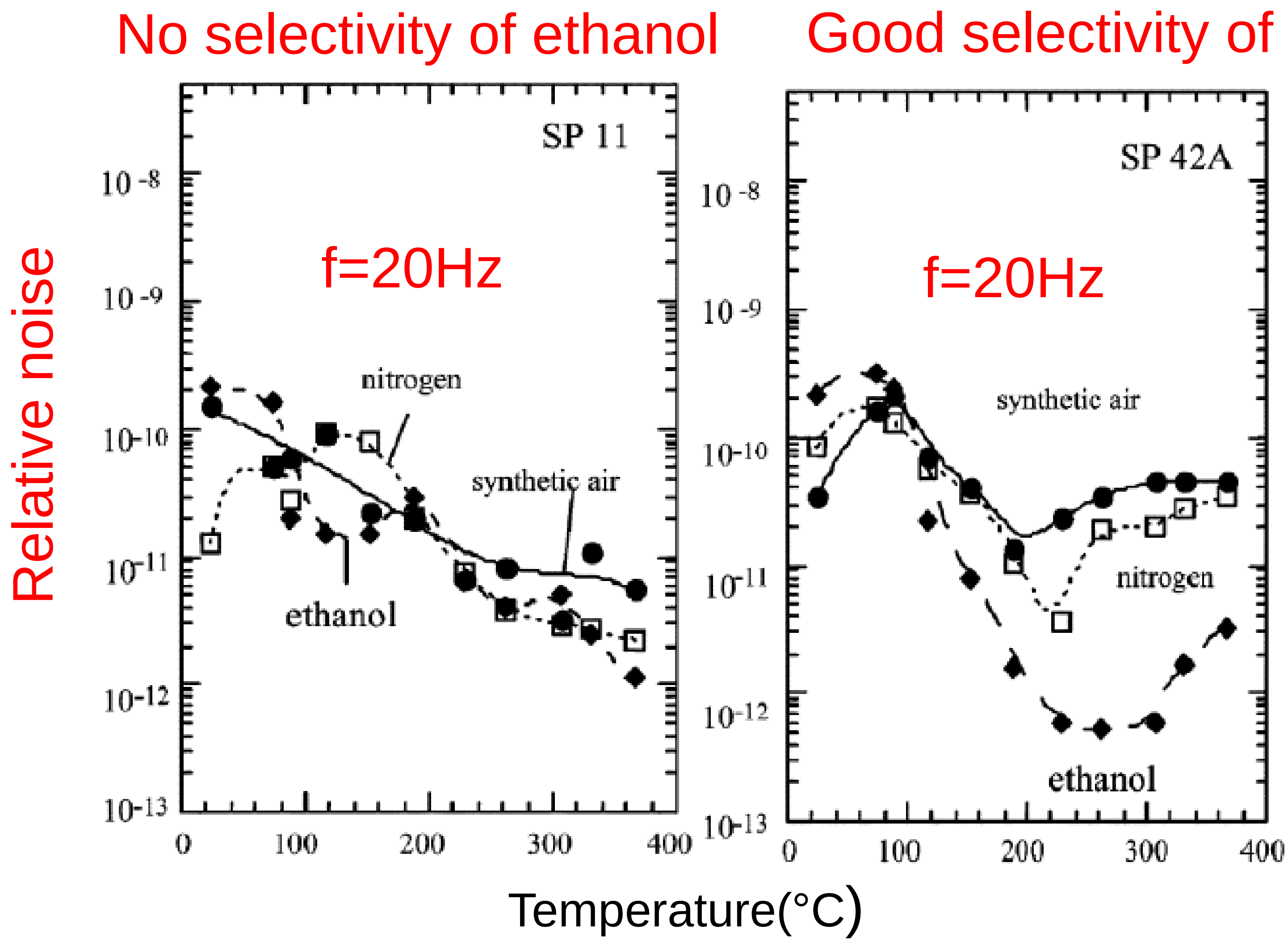
- Different Taguchi sensors (multigrain resistors)
- Temperature as control parameter
- power spectrum is not always correlated with changes in resistance

[Solis& I3E Sens. J., 5(2005)1338]

→1/f noise can be used for sensing too

$$\frac{S_R(T)}{R^2(T)} \approx R^m$$

1/f noise: selectivity of S_R/R^2 (T) vs. gas

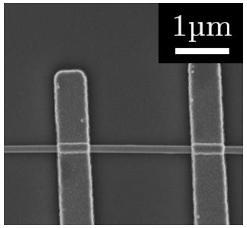


[Solis& I3E Sens. J., 5(2005)1338]

Taguchi sensor

- temperature dependence of 1/f noise magnitude can give an information on selectivity in some sensors
- Additional info to R(T)

Effect of humidity on 1/f noise in CuO NW



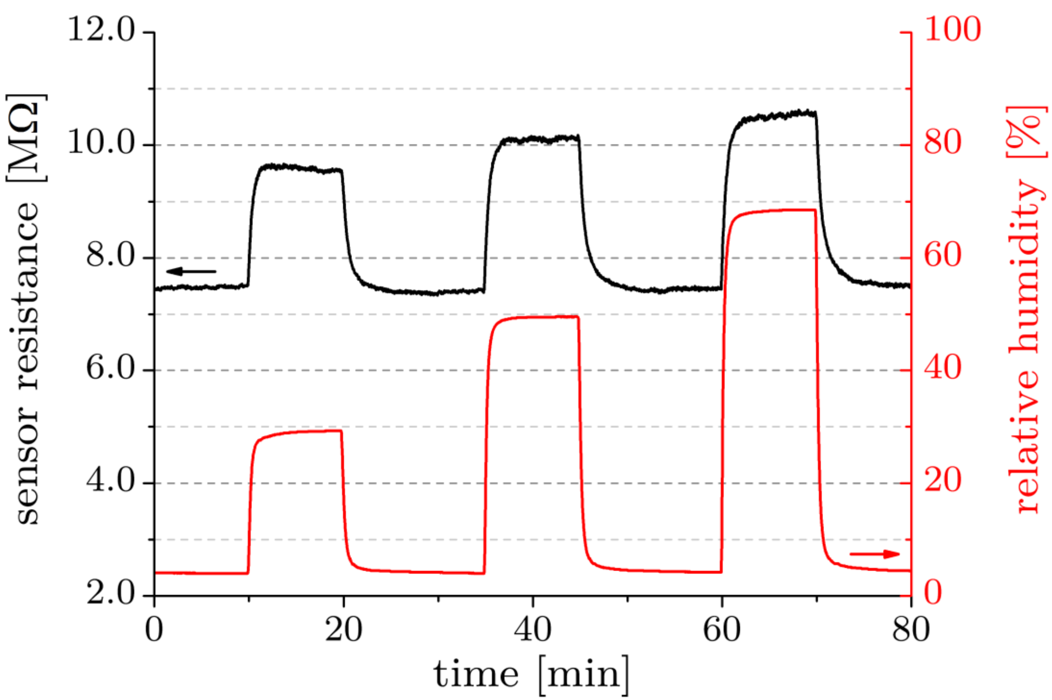
T=350°C, two-point configuration

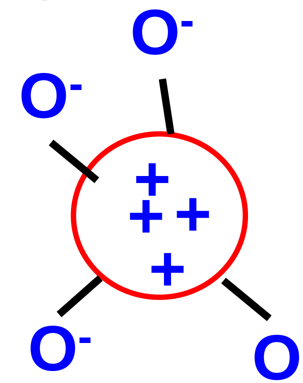
Relative humidity 0→50% (RH50)

[Steinhauer&, APL, 107(2015)122112]

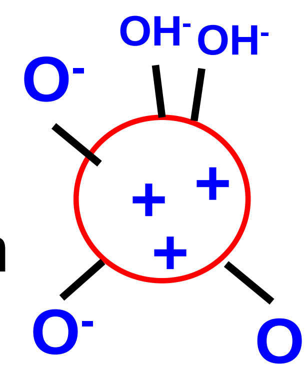
$$H_2O + O^-_{(ad)} + 2Cu_{Cu} + h^+ \rightarrow 2(Cu^+_{Cu} - OH^-) + S_O$$

Single crystals NW: p-type conductivity





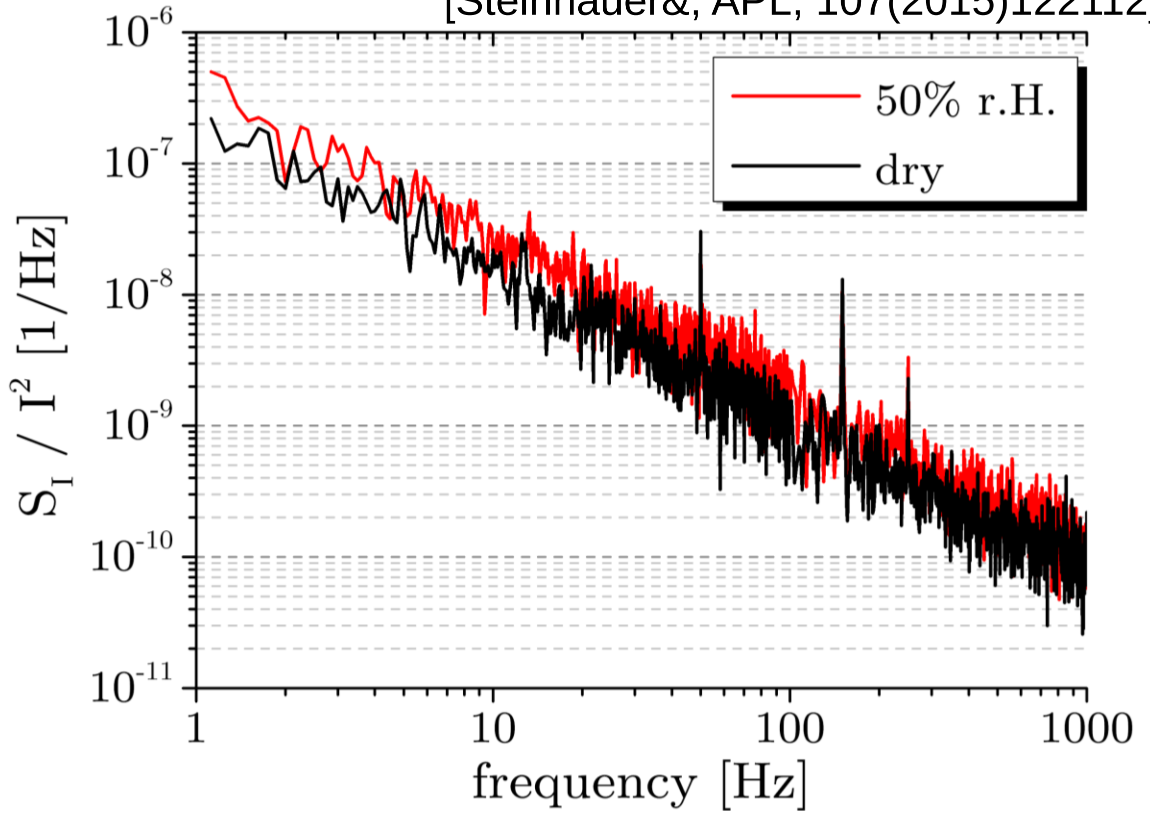
Water adsorption



- Humidity increases the resistance due to "compensation" of the negative surface charge by the hydroxyl group [M.Huebner& Sens. Act. B 153(2011)347-53]

1/f noise in CuO NW: effect of humidity

[Steinhauer&, APL, 107(2015)122112]



$$S_I = \frac{S_I(1Hz)}{f^a}$$

Here:

a ≅ 0.9-1.2

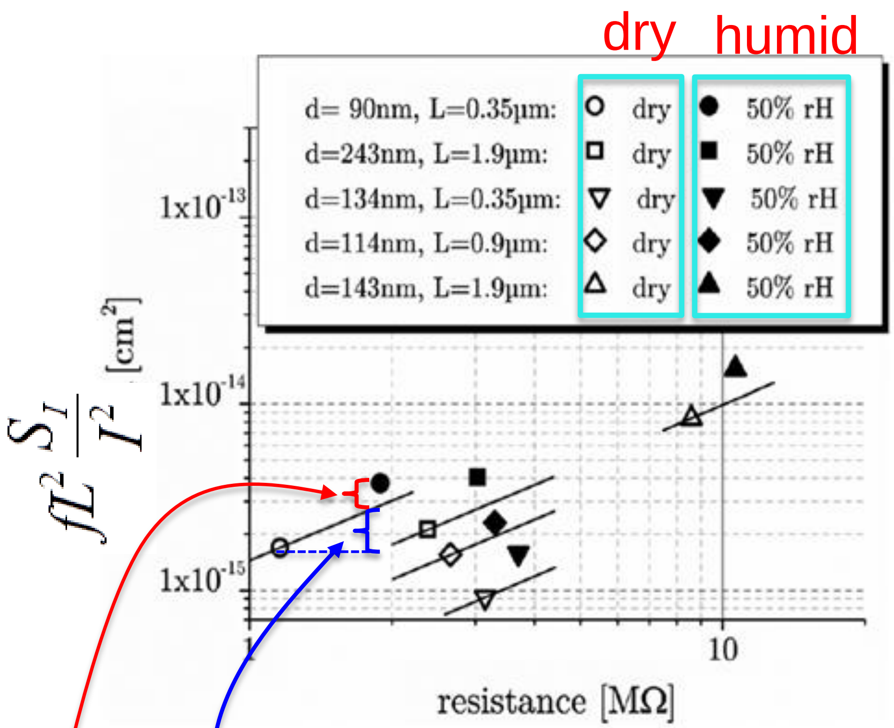
$$\frac{S_I}{I^2} = \frac{S_R}{R^2} = \frac{S_G}{G^2} = \frac{\alpha}{fN} = \frac{\alpha q \mu}{fL^2} R$$

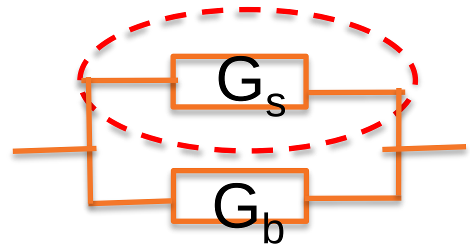
α-Hooge‘s noise coeff.
N-carrier number
μ-carrier mobility
q-element. charge
L - NW length

- 1/f noise found (no Lorentzians)
- Humidity increases the relative noise
- We consider mobility fluctuation model

1/f noise in CuO NW: effect of humidity

NWs of different dimensions





Core/shell model
s-surface
b-bulk

Only surface resistance and surface noise changes due to gas are considered!!!

$$\frac{S_R}{R^2_{TOT}} = \frac{S_{Gs} + S_{Gb}}{G^2_{TOT}} = \frac{\frac{\alpha_s}{N_s f} G_S^2 + \frac{\alpha_b}{N_b f} G_b^2}{(G_s + G_b)^2} = \frac{K_s G_s + K_b G_b}{fL^2 (G_s + G_b)^2},$$

Change due to total resistance change

Change due to rise in **surface** noise

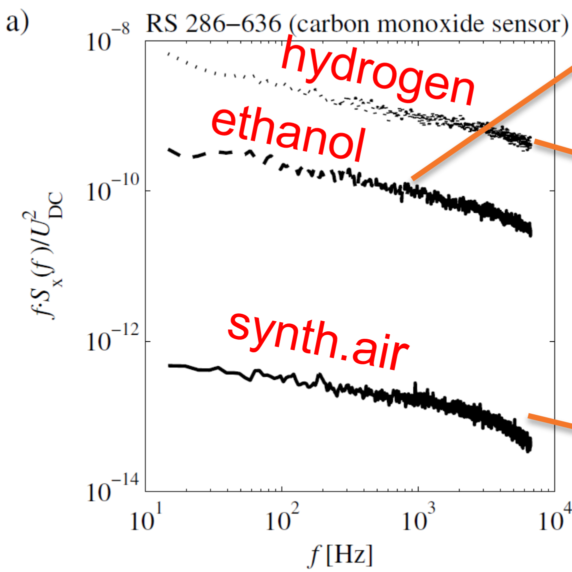
We consider fluctuations in scattering on surface potential roughness due to randomly distributed hydroxyl groups on NW surface

INOLOGY

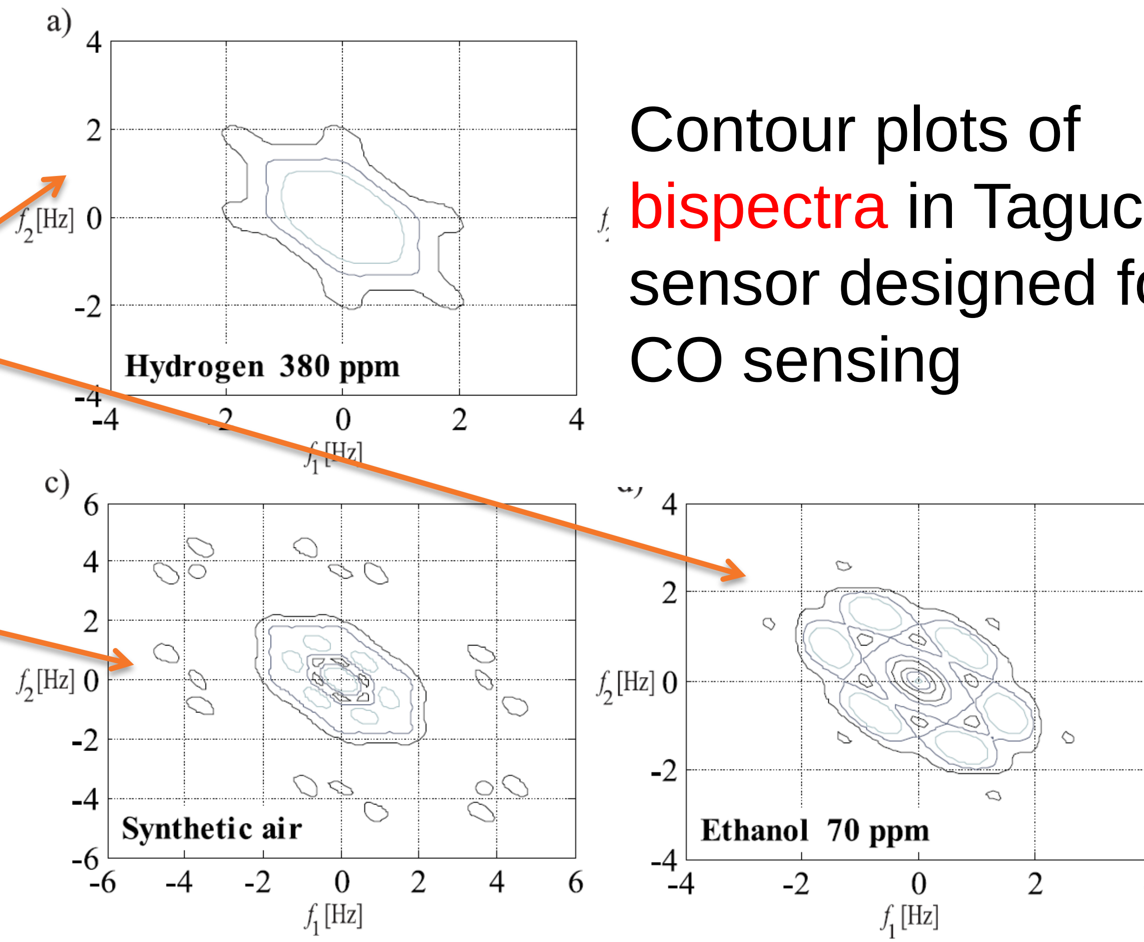
[Steinhauer&, APL, 107(2015)122112]

Higher order statistics-bispectrum

Power spectrum



[Smulko&, Sensors and Materials 16(2004)291]

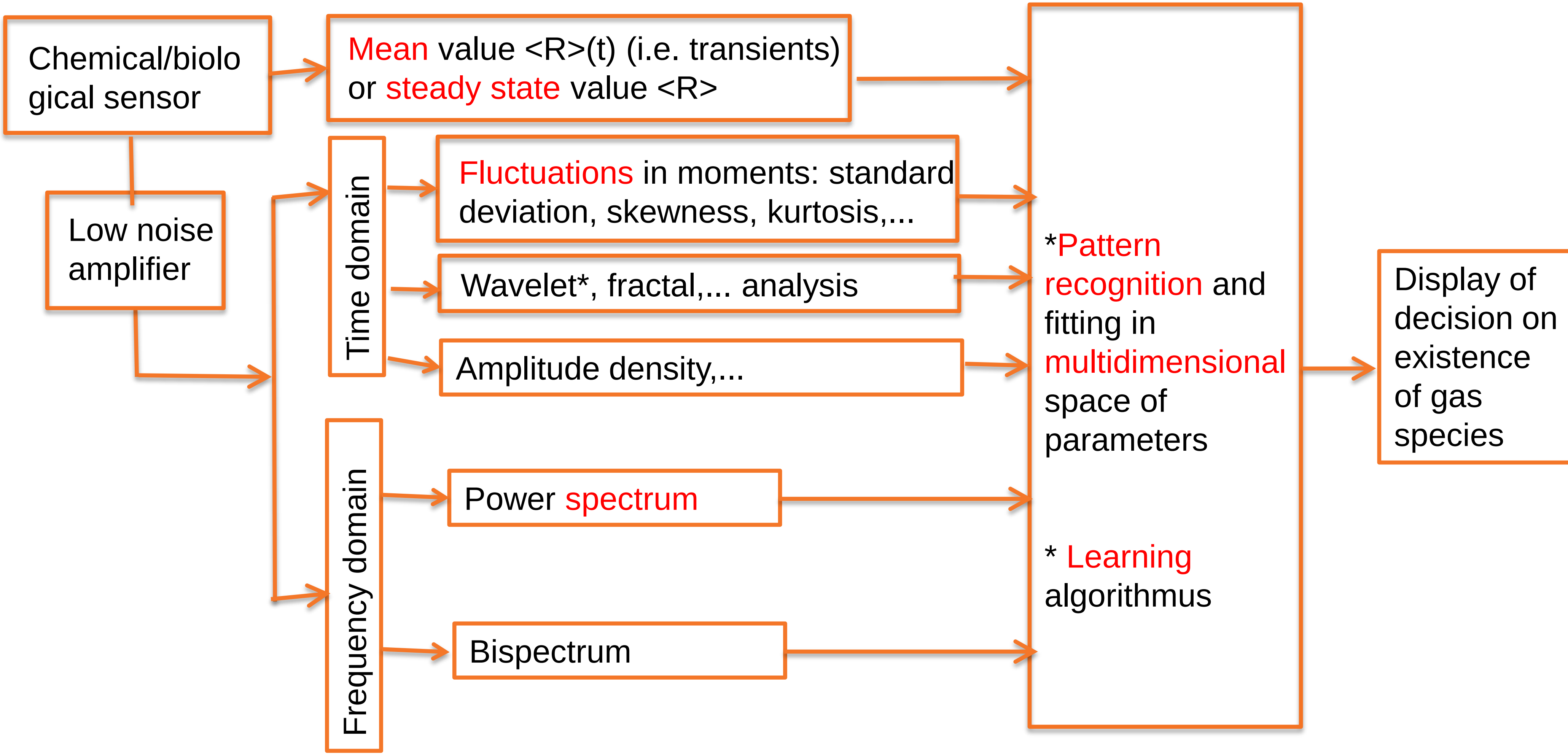


Contour plots of bispectra in Taguchi sensor designed for CO sensing

- special fingerprints of different gases in bispectra

$$S_{3x}(f_1, f_2) = \gamma_{3u} H(f_1) H(f_2) H^*(f_1 + f_2)$$

FES concept summary



Based on [Kwan& I3E Sens.J.,8(2008)706]: simplified + extended/updated

*Tulzer&, Nanotechnology 24(2013)315501

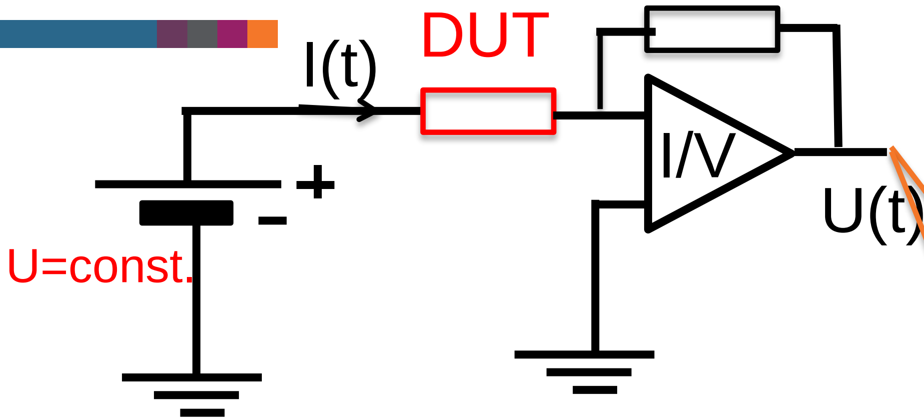
Precautions: What do we really measure?

- Defined measurement conditions:
- surface degasing prior to measurements
- besides measurement of frequency spectra, recording/analysis of time domain waveforms is strongly suggested
  - Not to misinterprete e.g. contact RTS noise as A/D noise
  - Stationarity: Drifts→1/f2 dependence
  - → Air and temperature fluctuations in measurement chamber and at the DUT should be low (laminar flow), [dT(t)→dR(t)]
- Spectral responses of different gases in a mixture are often not additive (training algorithm necessary) [Solis& I3E Sens.J.,5(2005,1338]
- Be careful in interpretations: even the noise mechanisms in “standard” electronic elements like resistors, FET, BJT,… are still in discussion→effects on sensor optimization strategy

Conclusions

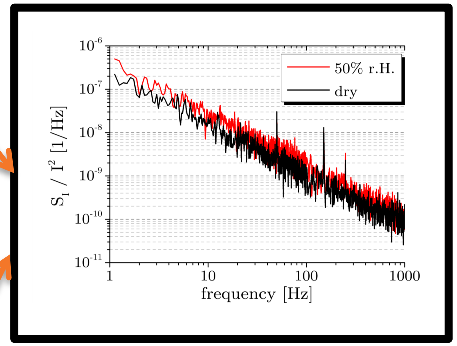
- Lorentzian-like and 1/f spectra can be used for gas sensing → additional information to <R> or <R>(t)
- Pure adsorption – desorption noise is not yet experimentally demonstrated in frequency domain
- Noise mechanisms in gas sensors are far from being understood!
- Precautions on measurements conditions

Noise measurements

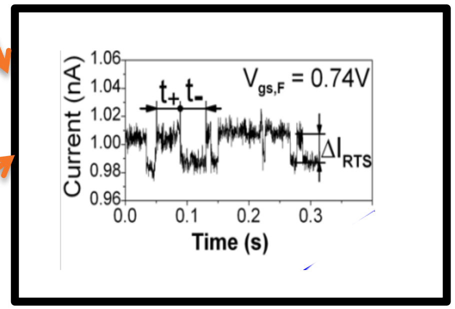


← Two point (contact noise and resistance included)

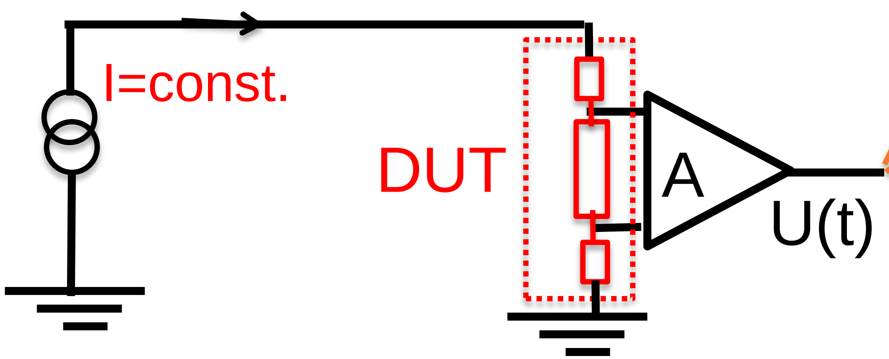
$$\frac{S_I}{I^2} = \frac{S_U}{U^2} = \frac{S_R}{R^2} = \frac{S_G}{G^2}$$



Spectrum analyzer: Freq. domain



Digital oscilloscope: Time domain



← Four points (contact noise and contact resistance not measured)

Supplement to 1/f noise in CuO NWs

$$\frac{S_R}{R^2}=\frac{S_{Gs}+S_{Gb}}{G^2}=\frac{\frac{\alpha_s}{N_s f}G_S^2+\frac{\alpha_b}{N_b f}G_b^2}{(G_s+G_b)^2}=\frac{K_sG_s+K_bG_b}{fL^2(G_s+G_b)^2},$$

$$\frac{K_bG_b+K_sG_s}{(G_b+G_s)^2}=\frac{K_b}{(G_b+G_s)}+\frac{G_s(K_s-K_b)}{(G_b+G_s)^2}=K_bR_{TOT}+G_s(K_s-K_b)R_{TOT}^2$$

$$\frac{1}{N_{s(b)}}=\frac{q\mu_{s(b)}R_{s(b)}}{L^2}$$

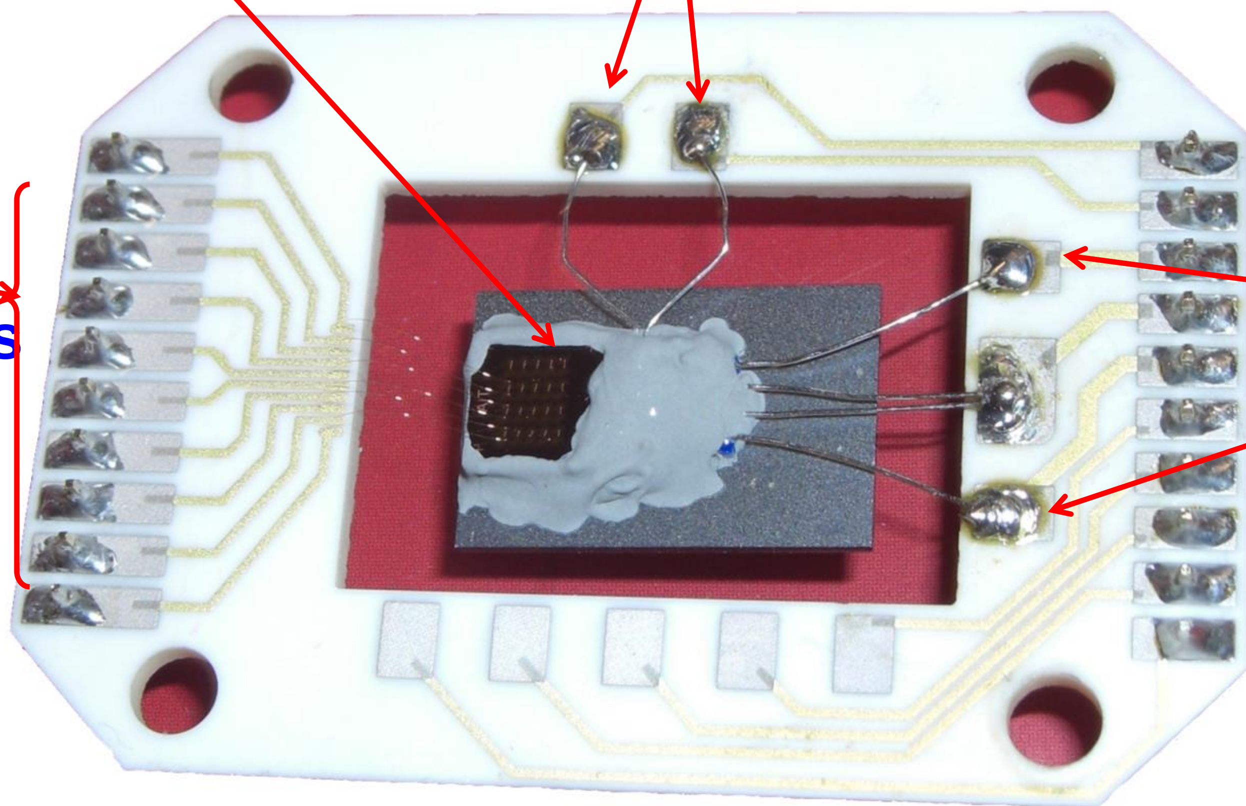
Ns(b): number of carriers in the surface (bulk) regions of NW
μ-mobilities
Ks(b)-coefficients
f-frequency
Gs(b)-surface (bulk) component of the conductance
RTOT=1/GTOT-total resistance

Test system

Chip with NWs

PT100 thermocouple

Bonded nanowires



Resistive heater element

- Temperatures up to 350°C
- Gas cell with controlled gas flow

Skewness and curtosis

Let us suppose that the $x(t)$ sensor signal is sampled and recorded as a time series $x(n)$. Simple measures of deviations[10] from Gaussian distribution are skewness, γ_3, and kurtosis, γ_4. These parameters are computed for a discrete-time random process $x(n)$ having standard deviation σ_x by the following relations:

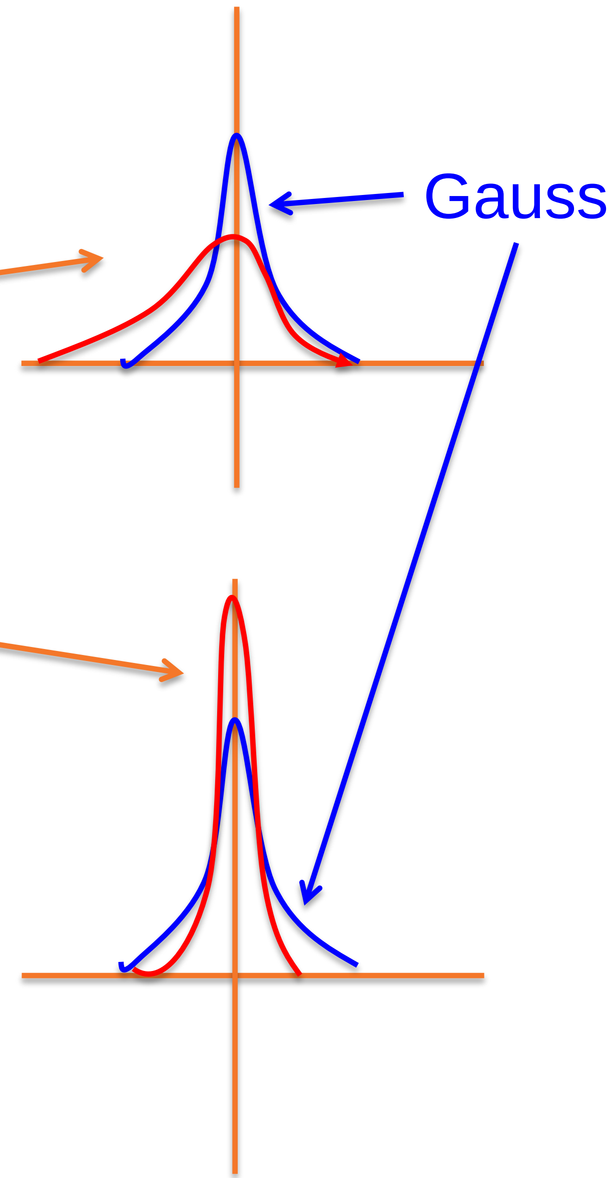
Skewness: assymetry

$$\gamma_3 = \frac{1}{\sigma_x^3} E\left[\left(x(n) - E[x(n)]\right)^3\right] \qquad (2)$$

Curtosis: peakness

$$\gamma_4 = \frac{1}{\sigma_x^4} E\left[\left(x(n) - E[x(n)]\right)^4\right] - 3 \qquad (3)$$

where $E[]$ denotes an average. The skewness describes the degree of symmetry and the kurtosis



Differences in respect to Gaussian amplitude distribution

5

[Smulko&, Sensors and Materials 16(2004)291]

measures the relative peakedness of the distribution. Both measures are equal to zero for a Gaussian process.

Bispectrum

[- axial symmetry of spectra → stationary process
- magnitude is near zero → the non zero values is due to a weak non-Gaussian component in the amplitude distribution]

[Kwan& I3E Sens.J.,8(2008)706

An important tool to investigate the non-Gaussian component of the stochastic sensor signal is the bispectrum[10-11]. The bispectrum function is the second-order Fourier transform of the third–order cummulant[11]:

$$S_{3x}(f_1,f_2) = \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} C_{3x}(k,l) e^{-j2\pi f_1 k} e^{-j2\pi f_2 l} \quad (4)$$

where $C_{3x}(k,l) = E[x(n)x(n+k)x(n+l)]$ is the third-order cummulant of the zero-mean process $x(n)$. The bispectrum is a two-dimensional complex function. Usually, its absolute value is analyzed, which is a three-dimensional landscape. The bispectrum function is equal to zero for processes with zero skewness, i.e. for Gaussian processes. The bispectrum of two statistically independent random processes equals the sum of the bispectra of the individual random processes. It is an important property of bispectra that Gaussian components in the recorded stochastic process are eliminated and only the non-Gaussian component are seen[11].

[Smulko&, Sensors and Materials 16(2004)291]

$$S_{2x}(f) = \gamma_{2u} \left| H(f) \right|^2 \quad (8)$$

$$S_{3x}(f_1, f_2) = \gamma_{3u} H(f_1) H(f_2) H^*(f_1 + f_2) \quad (9)$$

where $H(f)$ is the frequency response. It can be seen from (8) and (9) that the power spectrum does not carry any information about the phase of $H(f)$, while if $u(n)$ is non-Gaussian, the phase information can be recovered with the bispectrum.