Verifying the electrostatic theory of whiskers

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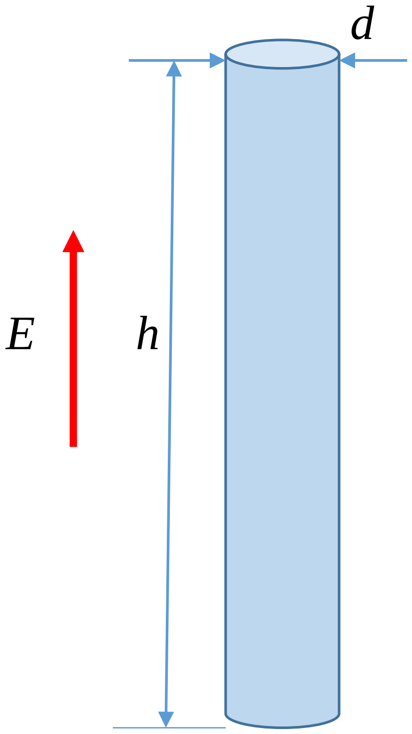
FIG. 1. Scanning electron microscope (SEM) pictures of tin (left) and zinc (right) whiskers. Courtesy of the NASA Electronic Parts and Packaging (NEPP) Program [6].

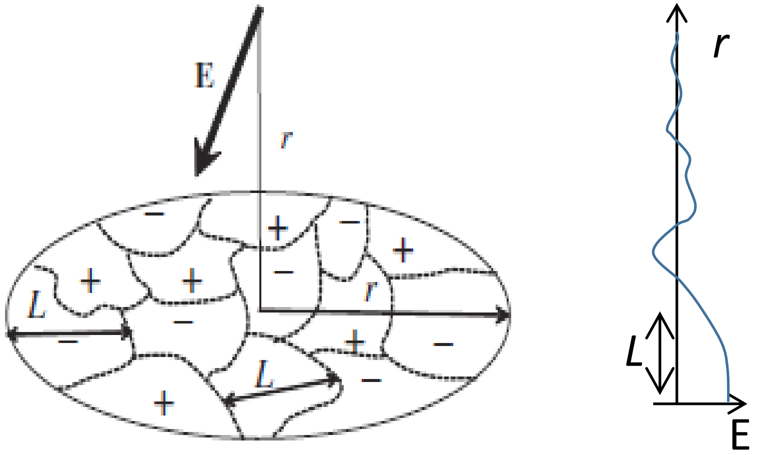
Electrostatic theory of metal whiskers in 1 slide



$$
\begin{aligned}
F &= \sigma h\pi d - pE = \\
&\sigma h\pi d - \beta E^2 \approx \\
&\sigma hd - h^3E^2 \approx \\
&\sigma hd - h^3E_0^2\left(L/h\right)^2 \approx \\
&(\sigma d - L^2E_0^2)h
\end{aligned}
$$

$$\alpha \equiv \frac{\sigma d}{E_0^2L^2}$$

σ-surface tension, $\beta \sim h^3$ – polarizability of a thin metal cylinder, *L* –linear size of a charged patch, E_0 is the near surface field at $h \ll L$.



# of patches seen from distance *r*, $N \sim (r/L)^2$.

Excess + or – charge felt $\propto \sqrt{N} \sim r/L \Rightarrow$

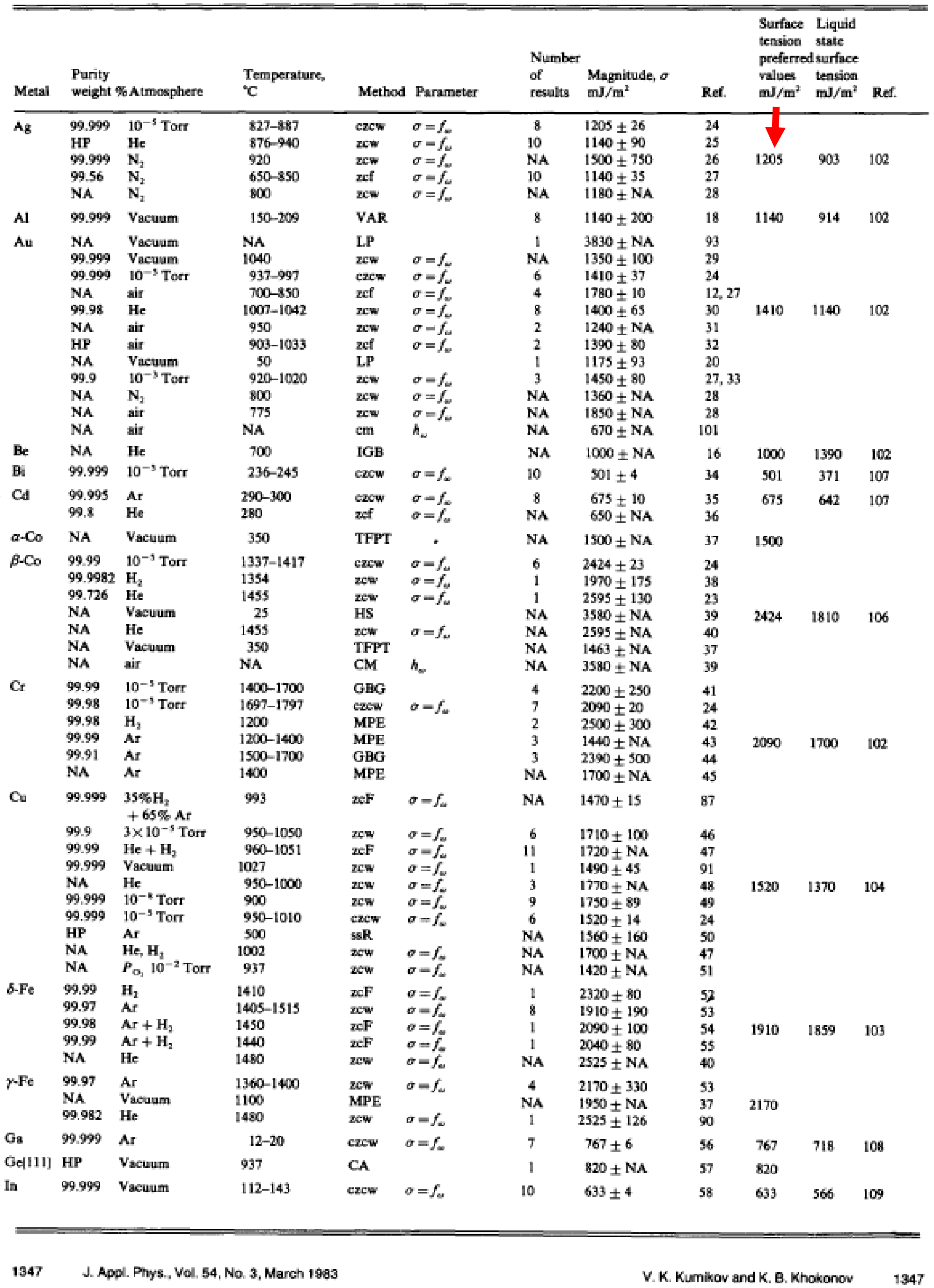
Absolute value of field $|E| \propto \frac{\sqrt{N}}{r^2} \sim |E_0|\frac{L}{r}$

α >>1 and probability of whiskering proportional to exp(-α)… (can be shown) –

-- Whiskers grow where a strong field fluctuation exists, which are rare, $\alpha \sim$ 10-100.

External E decreases α – **whisker propensity exponentially increases**

Lower surface tension decreases α – **whisker propensity exponentially increases**



Metal	Purity weight %	Atmosphere	Temperature, °C	Method	Parameter	Number of results	Magnitude, σ mJ/m^2	Ref.	Surface tension preferred values mJ/m^2	Liquid state surface tension mJ/m^2	Ref.
Ag	99.999	10^{-5} Torr	827–887	czcw	$\sigma = f_\omega$	8	1205 ± 26	24			
	HP	He	876–940	zcw	$\sigma = f_\omega$	10	1140 ± 90	25			
	99.999	N_2	920	zcw	$\sigma = f_\omega$	NA	1500 ± 750	26	1205	903	102
	99.56	N_2	650–850	zcf	$\sigma = f_\omega$	10	1140 ± 35	27			
	NA	N_2	800	zcw	$\sigma = f_\omega$	NA	1180 ± NA	28			
Al	99.999	Vacuum	150–209	VAR		8	1140 ± 200	18	1140	914	102
Au	NA	Vacuum	NA	LP		1	3830 ± NA	93			
	99.999	Vacuum	1040	zcw	$\sigma = f_\omega$	NA	1350 ± 100	29			
	99.999	10^{-5} Torr	937–997	czcw	$\sigma = f_\omega$	6	1410 ± 37	24			
	NA	air	700–850	zcf	$\sigma = f_\omega$	4	1780 ± 10	12, 27			
	99.98	He	1007–1042	zcw	$\sigma = f_\omega$	8	1400 ± 65	30	1410	1140	102
	NA	air	950	zcw	$\sigma = f_\omega$	2	1240 ± NA	31			
	HP	air	903–1033	zcf	$\sigma = f_\omega$	2	1390 ± 80	32			
	NA	Vacuum	50	LP		1	1175 ± 93	20			
	99.9	10^{-3} Torr	920–1020	zcw	$\sigma = f_\omega$	3	1450 ± 80	27, 33			
	NA	N_2	800	zcw	$\sigma = f_\omega$	NA	1360 ± NA	28			
	NA	air	775	zcw	$\sigma = f_\omega$	NA	1850 ± NA	28			
	NA	air	NA	cm	h_ω	NA	670 ± NA	101			
Be	NA	He	700	IGB		NA	1000 ± NA	16	1000	1390	102
Bi	99.999	10^{-3} Torr	236–245	czcw	$\sigma = f_\omega$	10	501 ± 4	34	501	371	107
Cd	99.995	Ar	290–300	czcw	$\sigma = f_\omega$	8	675 ± 10	35	675	642	107
	99.8	He	280	zcf	$\sigma = f_\omega$	NA	650 ± NA	36			
α-Co	NA	Vacuum	350	TFPT	.	NA	1500 ± NA	37	1500		
β-Co	99.99	10^{-3} Torr	1337–1417	czcw	$\sigma = f_\omega$	6	2424 ± 23	24			
	99.9982	H_2	1354	zcw	$\sigma = f_\omega$	1	1970 ± 175	38			
	99.726	He	1455	zcw	$\sigma = f_\omega$	1	2595 ± 130	23			
	NA	Vacuum	25	HS		NA	3580 ± NA	39	2424	1810	106
	NA	He	1455	zcw	$\sigma = f_\omega$	NA	2595 ± NA	40			
	NA	Vacuum	350	TFPT		NA	1463 ± NA	37			
	NA	air	NA	CM	h_ω	NA	3580 ± NA	39			
Cr	99.99	10^{-5} Torr	1400–1700	GBG		4	2200 ± 250	41			
	99.98	10^{-5} Torr	1697–1797	czcw	$\sigma = f_\omega$	7	2090 ± 20	24			
	99.98	H_2	1200	MPE		2	2500 ± 300	42			
	99.99	Ar	1200–1400	MPE		3	1440 ± NA	43	2090	1700	102
	99.91	Ar	1500–1700	GBG		3	2390 ± 500	44			
	NA	Ar	1400	MPE		NA	1700 ± NA	45			
Cu	99.999	35%H_2 + 65% Ar	993	zcF	$\sigma = f_\omega$	NA	1470 ± 15	87			
	99.9	3×10^{-5} Torr	950–1050	zcw	$\sigma = f_\omega$	6	1710 ± 100	46			
	99.99	He + H_2	960–1051	zcF	$\sigma = f_\omega$	11	1720 ± NA	47			
	99.999	Vacuum	1027	zcw	$\sigma = f_\omega$	1	1490 ± 45	91			
	NA	He	950–1000	zcw	$\sigma = f_\omega$	3	1770 ± NA	48	1520	1370	104
	99.999	10^{-8} Torr	900	zcw	$\sigma = f_\omega$	9	1750 ± 89	49			
	99.999	10^{-5} Torr	950–1010	czcw	$\sigma = f_\omega$	6	1520 ± 14	24			
	HP	Ar	500	ssR		NA	1560 ± 160	50			
	NA	He, H_2	1002	zcw	$\sigma = f_\omega$	NA	1700 ± NA	47			
	NA	P_{O_2}, 10^{-2} Torr	937	zcw	$\sigma = f_\omega$	NA	1420 ± NA	51			
δ-Fe	99.99	H_2	1410	zcF	$\sigma = f_\omega$	1	2320 ± 80	52			
	99.97	Ar	1405–1515	zcw	$\sigma = f_\omega$	8	1910 ± 190	53			
	99.98	Ar + H_2	1450	zcF	$\sigma = f_\omega$	1	2090 ± 100	54	1910	1859	103
	99.99	Ar + H_2	1440	zcF	$\sigma = f_\omega$	1	2040 ± 80	55			
	NA	He	1480	zcw	$\sigma = f_\omega$	NA	2525 ± NA	40			
γ-Fe	99.97	Ar	1360–1400	zcw	$\sigma = f_\omega$	4	2170 ± 330	53			
	NA	Vacuum	1100	MPE		NA	1950 ± NA	37	2170		
	99.982	He	1480	zcw	$\sigma = f_\omega$	1	2525 ± 126	90			
Ga	99.999	Ar	12–20	czcw	$\sigma = f_\omega$	7	767 ± 6	56	767	718	108
Ge[111]	HP	Vacuum	937	CA		1	820 ± NA	57	820		
In	99.999	Vacuum	112–143	czcw	$\sigma = f_\omega$	10	633 ± 4	58	633	566	109

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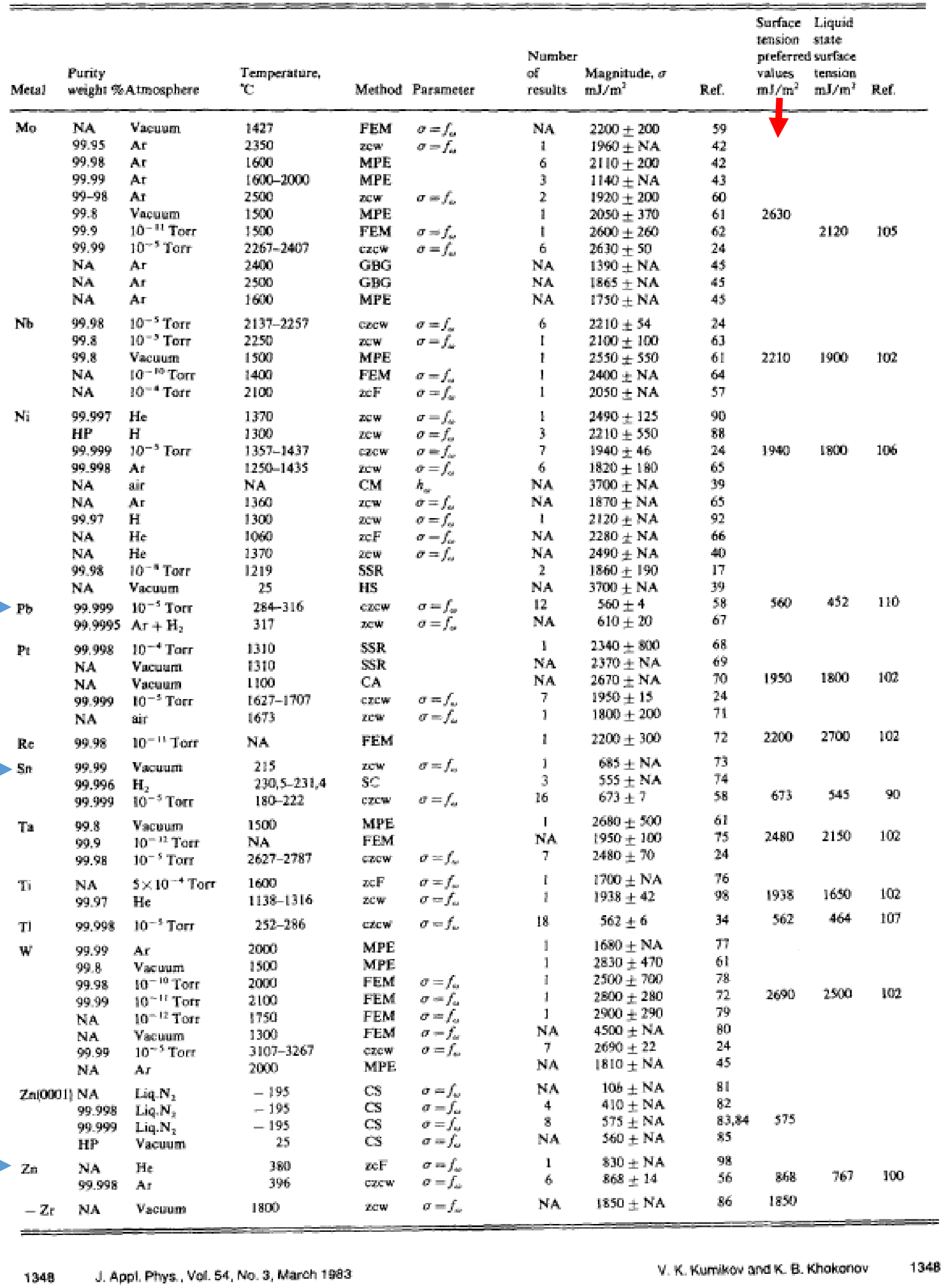

Metal	Purity weight %	Atmosphere	Temperature, °C	Method	Parameter	Number of results	Magnitude, σ mJ/m^2	Ref.	Surface tension preferred values mJ/m^2	Liquid state surface tension mJ/m^2	Ref.
Mo	NA	Vacuum	1427	FEM	$\sigma = f_\omega$	NA	2200 ± 200	59			
	99.95	Ar	2350	zcw	$\sigma = f_\omega$	1	1960 ± NA	42			
	99.98	Ar	1600	MPE		6	2110 ± 200	42			
	99.99	Ar	1600–2000	MPE		3	1140 ± NA	43			
	99–98	Ar	2500	zcw	$\sigma = f_\omega$	2	1920 ± 200	60			
	99.8	Vacuum	1500	MPE		1	2050 ± 370	61	2630		
	99.9	10^{-11} Torr	1500	FEM	$\sigma = f_\omega$	1	2600 ± 260	62		2120	105
	99.99	10^{-5} Torr	2267–2407	czcw	$\sigma = f_\omega$	6	2630 ± 50	24			
	NA	Ar	2400	GBG		NA	1390 ± NA	45			
	NA	Ar	2500	GBG		NA	1865 ± NA	45			
	NA	Ar	1600	MPE		NA	1750 ± NA	45			
Nb	99.98	10^{-5} Torr	2137–2257	czcw	$\sigma = f_\omega$	6	2210 ± 54	24			
	99.8	10^{-5} Torr	2250	zcw	$\sigma = f_\omega$	1	2100 ± 100	63			
	99.8	Vacuum	1500	MPE		1	2550 ± 550	61	2210	1900	102
	NA	10^{-10} Torr	1400	FEM	$\sigma = f_\omega$	1	2400 ± NA	64			
	NA	10^{-4} Torr	2100	zcF	$\sigma = f_\omega$	1	2050 ± NA	57			
Ni	99.997	He	1370	zcw	$\sigma = f_\omega$	1	2490 ± 125	90			
	HP	H	1300	zcw	$\sigma = f_\omega$	3	2210 ± 550	88			
	99.999	10^{-5} Torr	1357–1437	czcw	$\sigma = f_\omega$	7	1940 ± 46	24	1940	1800	106
	99.998	Ar	1250–1435	zcw	$\sigma = f_\omega$	6	1820 ± 180	65			
	NA	air	NA	CM	h_ω	NA	3700 ± NA	39			
	NA	Ar	1360	zcw	$\sigma = f_\omega$	NA	1870 ± NA	65			
	99.97	H	1300	zcw	$\sigma = f_\omega$	1	2120 ± NA	92			
	NA	He	1060	zcF	$\sigma = f_\omega$	NA	2280 ± NA	66			
	NA	He	1370	zcw	$\sigma = f_\omega$	NA	2490 ± NA	40			
	99.98	10^{-8} Torr	1219	SSR		2	1860 ± 190	17			
	NA	Vacuum	25	HS		NA	3700 ± NA	39			
Pb	99.999	10^{-5} Torr	284–316	czcw	$\sigma = f_\omega$	12	560 ± 4	58	560	452	110
	99.9995	Ar + H_2	317	zcw	$\sigma = f_\omega$	NA	610 ± 20	67			
Pt	99.998	10^{-4} Torr	1310	SSR		1	2340 ± 800	68			
	NA	Vacuum	1310	SSR		NA	2370 ± NA	69			
	NA	Vacuum	1100	CA		NA	2670 ± NA	70	1950	1800	102
	99.999	10^{-5} Torr	1627–1707	czcw	$\sigma = f_\omega$	7	1950 ± 15	24			
	NA	air	1673	zcw	$\sigma = f_\omega$	1	1800 ± 200	71			
Re	99.98	10^{-11} Torr	NA	FEM		1	2200 ± 300	72	2200	2700	102
Sn	99.99	Vacuum	215	zcw	$\sigma = f_\omega$	1	685 ± NA	73			
	99.996	H_2	230,5–231,4	SC		3	555 ± NA	74			
	99.999	10^{-5} Torr	180–222	czcw	$\sigma = f_\omega$	16	673 ± 7	58	673	545	90
Ta	99.8	Vacuum	1500	MPE		1	2680 ± 500	61			
	99.9	10^{-12} Torr	NA	FEM		NA	1950 ± 100	75	2480	2150	102
	99.98	10^{-5} Torr	2627–2787	czcw	$\sigma = f_\omega$	7	2480 ± 70	24			
Ti	NA	5×10^{-4} Torr	1600	zcF	$\sigma = f_\omega$	1	1700 ± NA	76			
	99.97	He	1138–1316	zcw	$\sigma = f_\omega$	1	1938 ± 42	98	1938	1650	102
Tl	99.998	10^{-5} Torr	252–286	czcw	$\sigma = f_\omega$	18	562 ± 6	34	562	464	107
W	99.99	Ar	2000	MPE		1	1680 ± NA	77			
	99.8	Vacuum	1500	MPE		1	2830 ± 470	61			
	99.98	10^{-10} Torr	2000	FEM	$\sigma = f_\omega$	1	2500 ± 700	78			
	99.99	10^{-11} Torr	2100	FEM	$\sigma = f_\omega$	1	2800 ± 280	72	2690	2500	102
	NA	10^{-12} Torr	1750	FEM	$\sigma = f_\omega$	1	2900 ± 290	79			
	NA	Vacuum	1300	FEM	$\sigma = f_\omega$	NA	4500 ± NA	80			
	99.99	10^{-5} Torr	3107–3267	czcw	$\sigma = f_\omega$	7	2690 ± 22	24			
	NA	Ar	2000	MPE		NA	1810 ± NA	45			
Zn(0001)	NA	Liq.N_2	− 195	CS	$\sigma = f_\omega$	NA	106 ± NA	81			
	99.998	Liq.N_2	− 195	CS	$\sigma = f_\omega$	4	410 ± NA	82			
	99.999	Liq.N_2	− 195	CS	$\sigma = f_\omega$	8	575 ± NA	83,84	575		
	HP	Vacuum	25	CS	$\sigma = f_\omega$	NA	560 ± NA	85			
Zn	NA	He	380	zcF	$\sigma = f_\omega$	1	830 ± NA	98			
	99.998	Ar	396	czcw	$\sigma = f_\omega$	6	868 ± 14	56	868	767	100
− Zr	NA	Vacuum	1800	zcw	$\sigma = f_\omega$	NA	1850 ± NA	86	1850		

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Summary. Food for thought.

$$P \propto \exp\left(-\frac{const \times \sigma}{E_0^2 + 2EE_0(h/L) + E^2(h/L)^2}\right)$$

external field dominated when

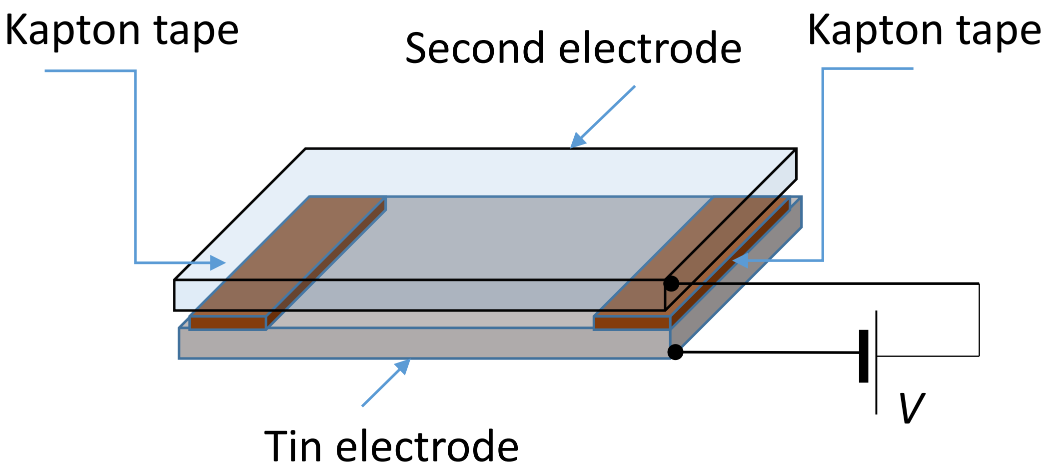
$E \geq E_0 L/(h\alpha)$.

Additionally, nucleation rate can be presented as

$$\exp\left(-\frac{const \times \sigma^2}{E_0 + E}\right)$$ (derived earlier -- 2009)

Correlation with σ seems obvious from the table.
Do we have correlations with E? – Preliminary YES – from two groups now
Other thoughts?
Changing σ by affecting interfaces (contaminations)?
Studying E-dependences more quantitatively?

‘Standard’ E-field test design for our and other groups



- Flat plate capacitor design:
- Thickness of kapton tape (spacer) $h = 25$ μm
- Voltage V=100 Volt
- Creates field $E= V/h=40{,}000$ V/cm
- Expect several-micron-long whiskers in several hours (say, 5 μm long whiskers in 5 hours for our used sputtered Sn films)
- If whiskers are not observed, check ‘craters’ caused by burned whiskers on the tin electrode
- Adding contaminations on the tin electrode will allow to see possible effects in hours
- Putting a polymer or other capping layer on tin will allow to study its whisker blocking effect in hours

We will use this setup with various films (tin and others) and with tin crystals. Other groups are welcome to exchange the results and samples. This setup can be developed into an industrial test.

Appendix 1: My compressed bullet points for a theory

(in blue what we have understood already in the electrostatic ctheory)

- A mystery of high aspect ratios, height/diameter up to ~10,000 not seen in other physics. Why would not metal whiskers collapse into ‘spheres’, as other droplets do to minimize surface energy?
- Is their relation to metals of essence? In other words, why are metal whiskers metal?
- What is behind the metal whiskers randomness? Why do they grow here but not there, why are their parameters so dispersed, what makes it so difficult to controllably grow or predict their appearance?
- What does Pb do in suppressing whiskers? (Either increases the surface tension or levels out the surface charge fluctuations)

Appendix 2: Gordon Davy’s amazing bullet points

- Nominally identical specimens may demonstrate drastically different densities and growth rates.
- Density may differ greatly from one region of a specimen to another; on a finer scale, there is a whisker growing *here*, but not *there*. So there is a minimum surface area needed to establish consistent density values.
- Growth is at the base (i.e., the film), not the tip.
- Growth may be from the tin-substrate interface or from near the tin surface.
- Growth rate is often not constant. A whisker may stop growing for a while, then start growing again.
- Growth rate is zero at low and high temperatures, and seems to peak at about 25-50°C.
- Growth can be promoted by thermal cycling (for tin on alloy 42, due to induced stresses from differential expansion).
- Growth rate is zero below a threshold film thickness and approaches zero for high film thickness. It appears to be zero for bulk tin.
- For sputtered films, growth rate appears to be a minimum for near-zero residual stress, and greater for tensile as well as compressive stress. (Bozack)
- Growth rate is somewhat higher at high humidity.
- Growth rate seems to be higher from fine-grained microstructure.
- Growth rate can be increased by some kinds of residues on the surface.
- Most metals dissolved in tin appear to increase growth rate. The one exception is Pb. The mechanism may have to do with altering the grain structure to equiaxed (from columnar).
- I do not recall hearing of the effect of small amounts of Pb (~1%) in Sn for vapor-deposited films, or even for very thin electroplated films.
- Distribution of thickness and length are log-normal.

Gordon Davy's amazing bullet points (continued)

- There appears to be no correlation between thickness and length.
- Median thickness is about 3 µm.
- Longest whisker reported: ~25 mm.
- Thinnest and thickest whiskers reported: ~100 nm, ~20 µm.
- Various growth morphologies: needle-like, "odd-shaped eruptions," occasional branches, there may longitudinal or circumferential striations. Acicular (needle-like) whiskers may be bent or kinked, and may not have the same thickness along the entire length.
- Long whiskers are in constant motion in air (due to natural convection) – can be compared to Brownian motion of airborne particles.
- Whiskers have an oxide coating ~1-3 nm thick, even in vacuum. (Growth rate is logarithmic.)
- A whisker that melts exits the skin, leaving it behind.
- Whiskers penetrate even a thick oxide film (grown by prolonged exposure to steam). (Bozack)
- Whiskers eventually penetrate polymer (including Parylene) coatings (with the apparent exception of "Whisker-tough." A polymer's resistance to penetration surely depends on temp, humidity, and age, but there are no data.
- Whiskers appear to not penetrate thin caps of certain metals, and readily penetrate thicker caps of other metals. (Bozack, Chason, Davy)
- Whiskers appear to not penetrate thin films of tailored ceramics produced by chemical vapor deposition *if* the substrate has been properly prepped. If the ceramic film is too thin, it is vulnerable to abrasion; too thick, to crazing and loss of adhesion due to differential expansion.