Fresh NRG Workshop

Rapperswil 20th March

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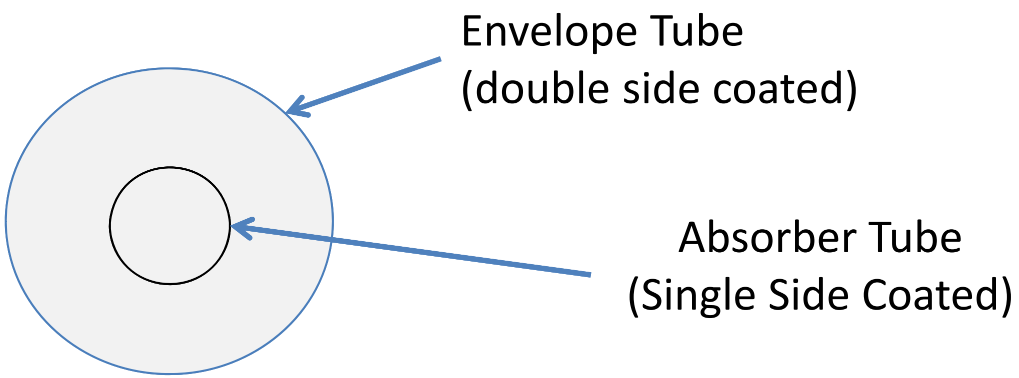
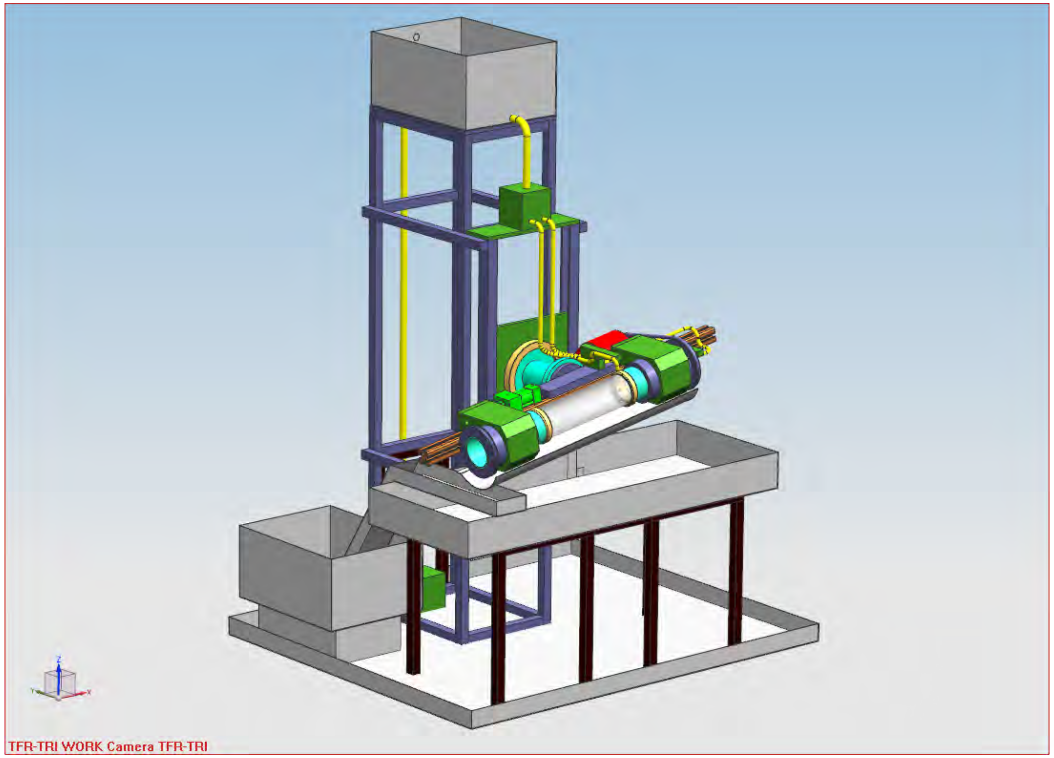
Overview(1)

- Developing coatings for receiver tube using sol-gel methods.
- Current aims are:
  - Sol Gel Anti-reflection coatings (ARC) for 96% transmittance for the glass envelope
  - Sol Gel selective absorptance coatings for 95% absorptance and 7% emittance at 250°C for the absorber tube.



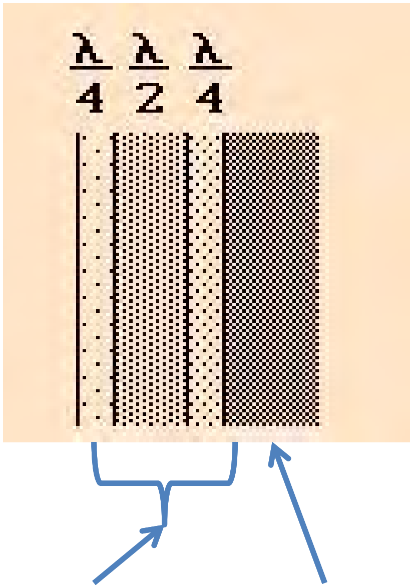
Overview(2)

Design and develop a tube coating machine capable of utilising the developed SOLS.



ARC Coating

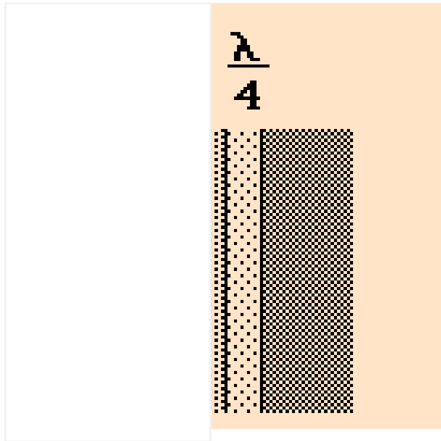
Initial Idea for the ARC described in the DoW



Substrate

3 different n-values
(multiple layers)

Present Approach



Driven by attempt to simplify manufacture process and aid tube throughput

ARC Coating

Two different approaches for Silica Based Coatings

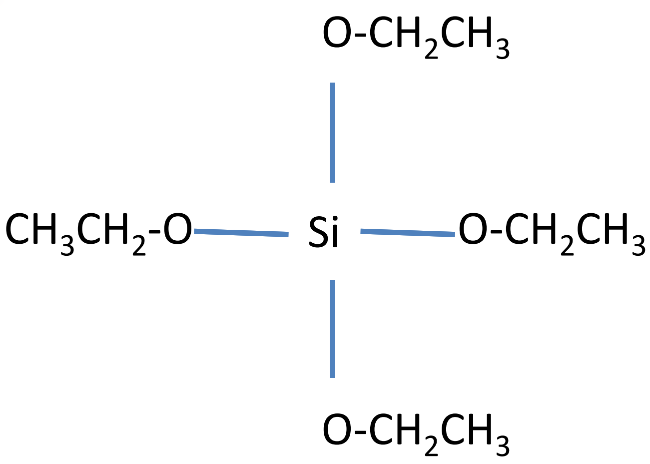
•MTES(ethanol/water/Propanol-acid hydrolysed based)(Primarily intended for the 3 layer ARC)

•MTES or TEOS (ethanol-base hydrolysed based)

What is MTES or TEOS

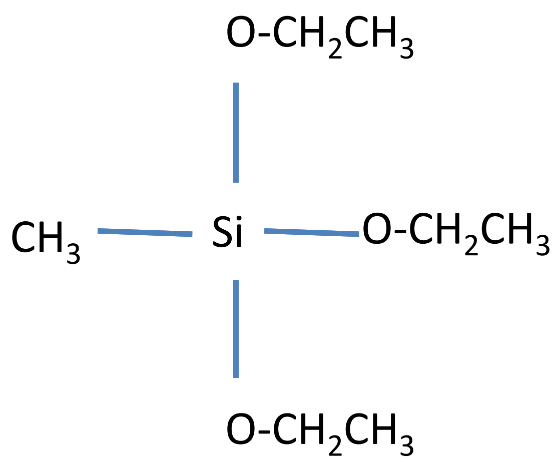
Silica Source

TEOS



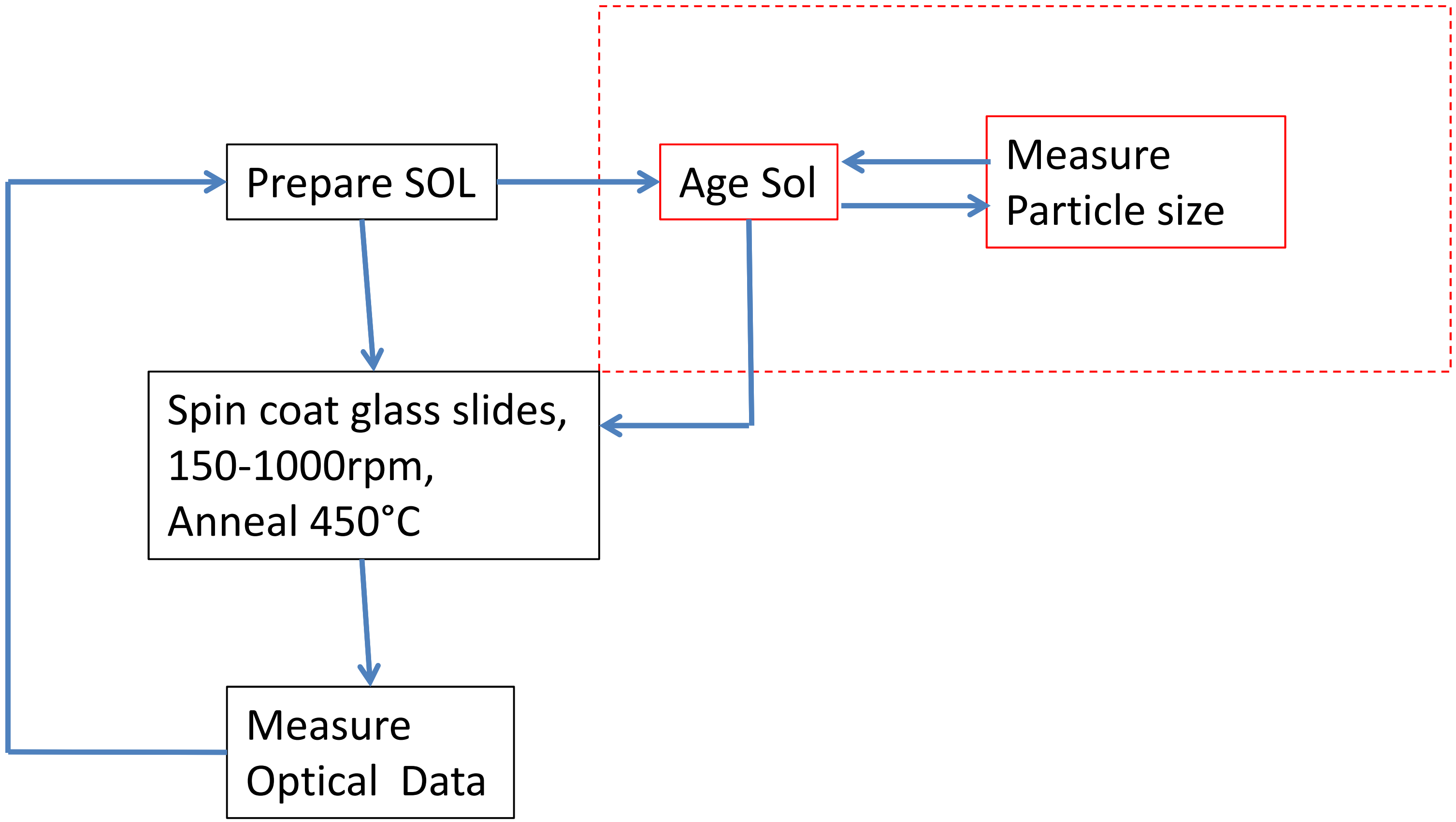
(Tetraethoxysilane)

MTES



(Methyl triethoxysilane)

SOL Optimisation routes



MTES acid catalysed Hydrolysis

(MTES- Methyl triethoxysilane)

Initial drive to use MTES was:

- To form a silica film as part of a 3 layer ARC
- Less hazardous than TEOS(which has been used for silica particle synthesis)
- The methyl group offers hydrophobic properties.
- An initial formulation incorporating water as part of the sol system could be devised.

Subsequently a sol formulation(MTES-1) has developed:

MTES/H20/Ethanol/Propan-2-ol/HCl

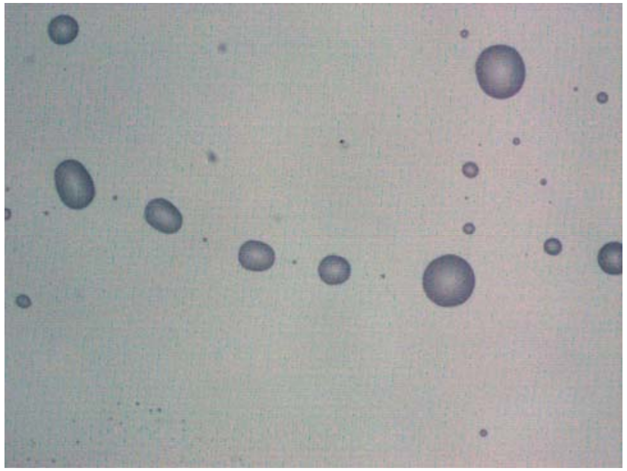
Mix Water and Ethanol. Add MTES stirring.
Dilute with Propan-2-ol and filter.
Add the HCl and stir for 1hr.

NOTE: the water content represents only 10% of the SOL and the addition of the propanol aids the wetting of the glass substrate)

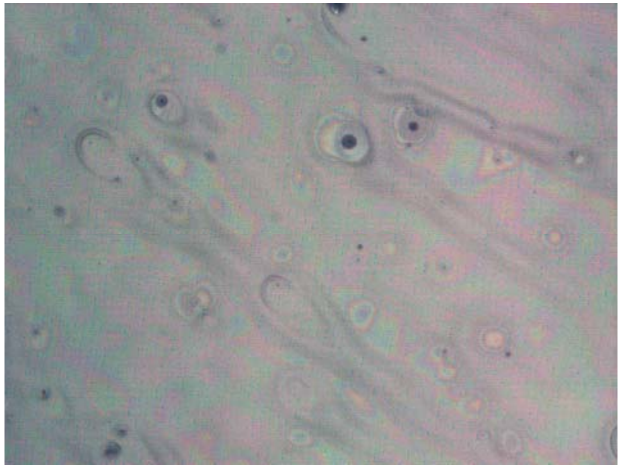
MTES-1 Sol Properties

Unactivated shelf life >2months
Activated Shelf Life Evidence: up to 8 day
Wettability of substrate

MANUFACTURABILITY



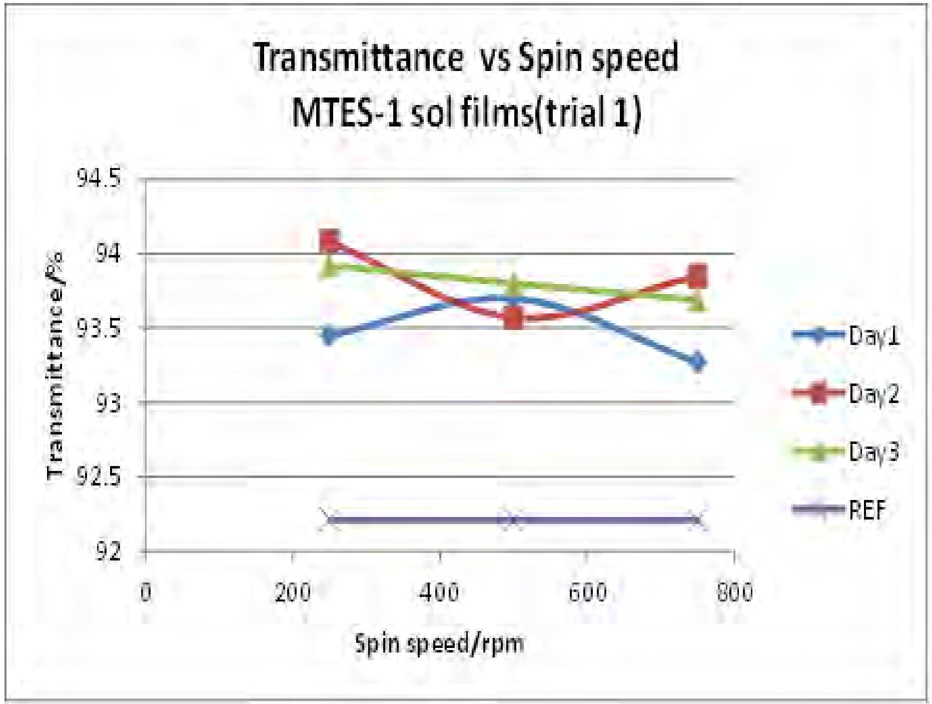
Non-Activated Sol Coating
(non-wetting)



Activated Sol Coating
(Improved wetting)

MTES-1 Derived Film Properties

Optimum single side coated transmission-93.2%
Optimum double side coated transmission-94.0%



Double sided coating
Trials Transmission
Data

ARC sol gel coatings

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- The measured transmission characteristics of the sols have been compared to an earlier set of MTES sols (trial 1) and provide further support to the fact that neither:
  - Spin speeds – 250, 500 and 750rpm.
  - Operator - (two sets of sols prepared by a different operator).
  - Age of sol - (Trial 1: sol was activated after day 1, day2 and day 3. Trial 2: sol was activated after day 5, day 6 and day 7).

affect the transmission characteristics. **<u>The sol is robust from a manufacturing</u> viewpoint**.

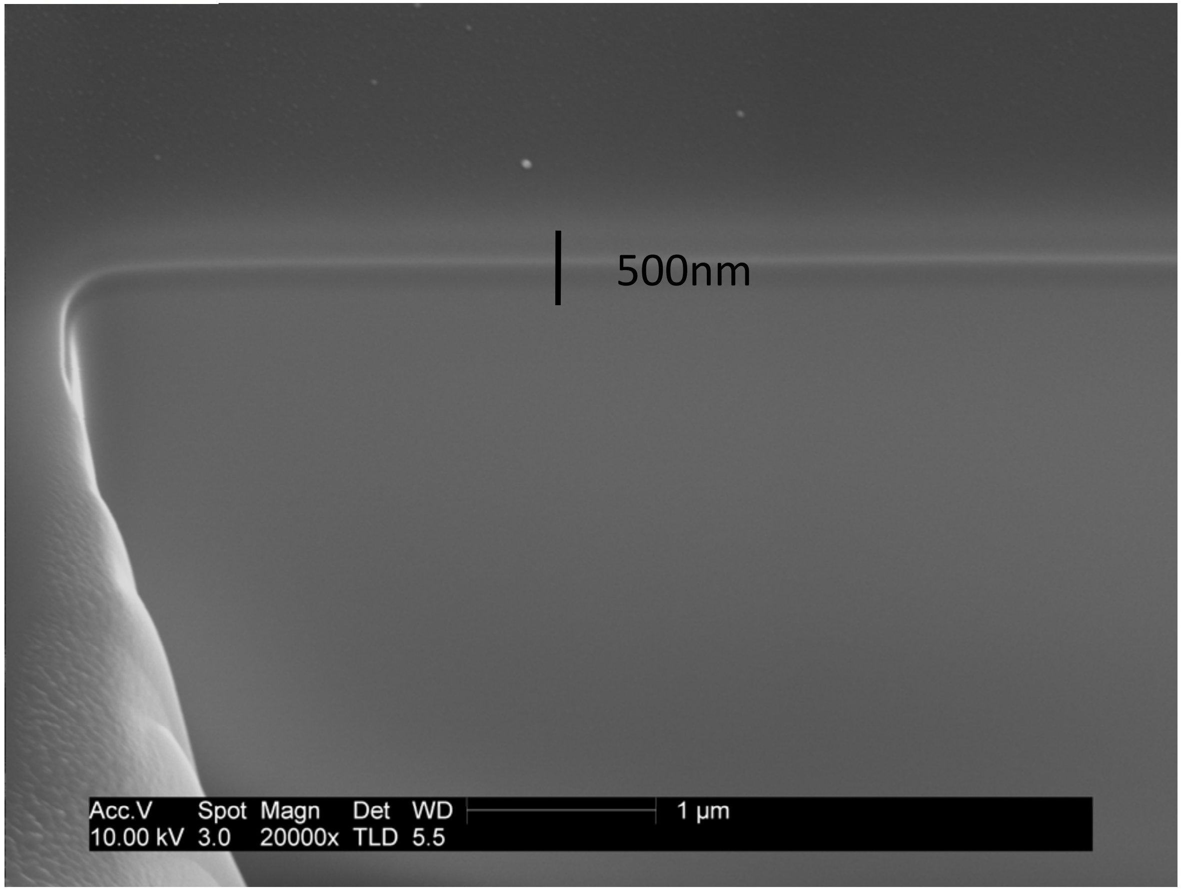
Sample ID	Batch	Spin Speed (rpm)	Transmittance (CU)	Transmittance (SPF)
Si20	Day1	750	93.30%	93.50%
Si21	Day1	500	93.70%	93.90%
Si22	Day1	250	93.50%	93.60%
Si26	Day2	750	93.90%	94.20%
Si27	Day2	500	93.60%	94.10%
Si28	Day2	250	94.10%	93.90%
Si32	Day3	750	93.70%	93.90%
Si33	Day3	500	93.80%	94.00%
Si34	Day3	250	93.90%	93.90%
Average			**93.72%**	**93.89%**

Sample ID	Batch	Spin Speed (rpm)	Transmittance (CU)	Transmittance (SPF)
Si50	Day5	250	93.90%	93.90%
Si51	Day5	500	93.90%	93.90%
Si52	Day5	750	93.90%	93.90%
Si54	Day6	250	94.00%	93.90%
Si55	Day6	500	93.10%	93.90%
Si56	Day6	750	93.20%	94.00%
Si57	Day7	250	94.00%	93.90%
Si58	Day7	500	93.50%	93.90%
Si59	Day7	750	93.70%	94.00%
Average			**93.69%**	**93.92%**

Dektak Profilometer Measurements of Scratched Film

CODE	Spin Speed/RPM	Thickness/nm[1]	Typical peak Trough measurement/nm[2]	RA/nm
Si-57	250	453, 415	120, 80	18, 19
Si-58	500	261, 266	190, 38	57, 39
Si-59	750	168, 156	27, 61	21, 25

[1]Two measurements made at a point halfway between centre and edge of glass slide,
[2]Typical peak to trough measurement estimated to indicate surface topology. For RA trace length is 3mm.



SEM Image tends to confirm a dense structure to the film which is difficult to distinguish from the substrate)

FIB-SEM image (30º tilted) of MTES1 (acid catalysed) sample Si-57

Rough dektak measurement of this film was ~430nm

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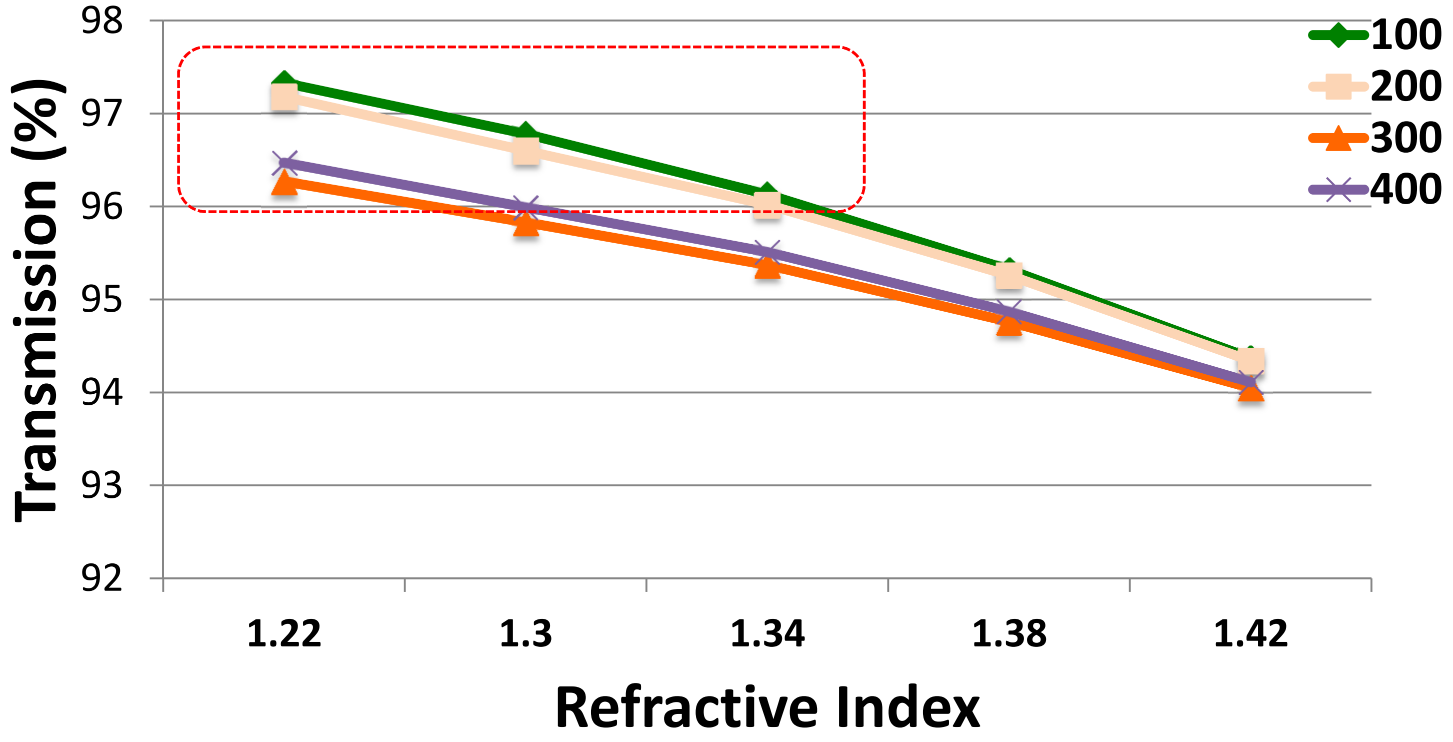
R. index	Thickness (nm)	Transmittance (Single sided)	Transmittance (Double sided)
1.42	106	93.68	94.37
	212	93.66	94.34
	318	93.52	94.05
	424	93.55	94.11
1.38	**109**	**94.15**	**95.32**
	218	94.11	95.26
	327	93.88	94.76
	436	93.93	94.87
1.34	**112**	94.54	**96.13**
	224	94.48	96.02
	336	94.17	95.37
	448	94.23	95.51
1.30	**115**	94.85	**96.78**
	230	94.76	96.60
	345	94.38	95.83
	460	94.47	95.99
1.22	**123**	**95.11**	**97.33**
	246	95.03	97.18
	369	94.59	96.27
	492	94.7	96.47

Quoted thicknesses are QWOTs*

Model: Single Layer Silica based AR Coating

Modelling: Sensitivity of the RI & thickness to the double-sided transmission characteristics



Refining the modelling of a single AR coating on glass we find that:
RI ≤ 1.30 would produce 96% transmission, with coating thicknesses of up to 460nm*
RI ≤ 1.34 would produce 96% transmission, with coating thicknesses of up to 200nm

2-layer ARC modelling

R. Index (n) (2-materials)	Thickness (nm)	Transmittance (Single sided)	Transmittance (Double sided)
1.44/**1.38** **(silica +MgF_2)**	**200/200**	94.04	**95.09**
	250/250	93.99	94.99
	400/400	93.96	94.94
1.44/1.22 (silica + low index material)	**200/200**	95.13	**97.38**
	250/250	94.96	97.01
	400/400	94.83	96.75

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Base Hydrolysed Route

Literature indicates potential route for:

•controlled particle size within the sol

•low refractive index films –n=<1.30

Drive to move to the Base catalysed route was:

• Modelling Directed to Achieve lower refractive index films.
•Potential for a simple Ethanol based route.

Base catalysed route is based on the Stober Method, and the formulations attempted so far have drawn from the following reference:

Guangming et al. Mat. Science and Eng. B78(2000) 135-139.

Guangming et al. Mat. Science and Eng. B78(2000) 135-139.

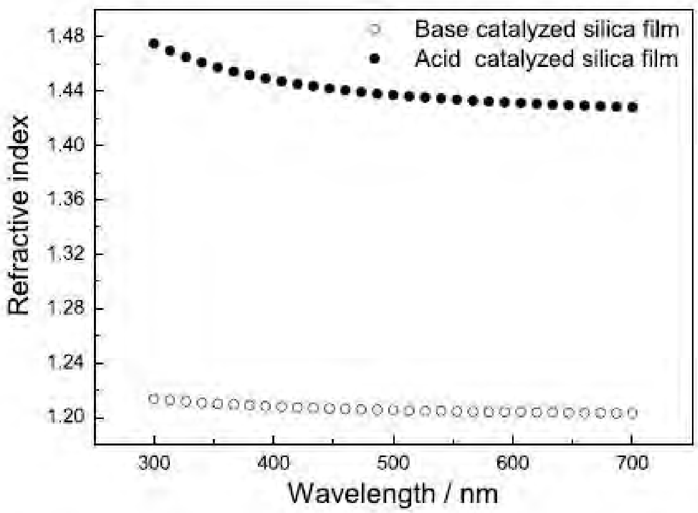

Fig.3 Optical constants of the silica film *via* sol-gel process with base catalysis and acid catalysis

Paper prepares films using the base and catalysed routes using TEOS as the Silica source to show variation in refractive index.

Synthesis route involves 5-7 day aging /stirring of the reactants followed by a reflux step.

A multiple dip coating route used to prepare the films for the optical analysis.

MTES-1 results to date seem consistent with the refractive index indicated above for the acid catalysed films

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Porous Silica (via Base hydrolysed route (Stober Process))

MTES/Ethanol/NH3.H20 (1:25:1-2 molar ratio)
TEOS/Ethanol/NH3.H20 (1:40:1-2 molar ratio)

MTES or TEOS mixed with Ethanol.

↓

Ammonia added dropwise with stirring.

↓

The mixture is then **aged** for 3-10 days.

↓

Reflux to drive off ammonia.

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MTES /TEOS Base catalysed Hydrolysis

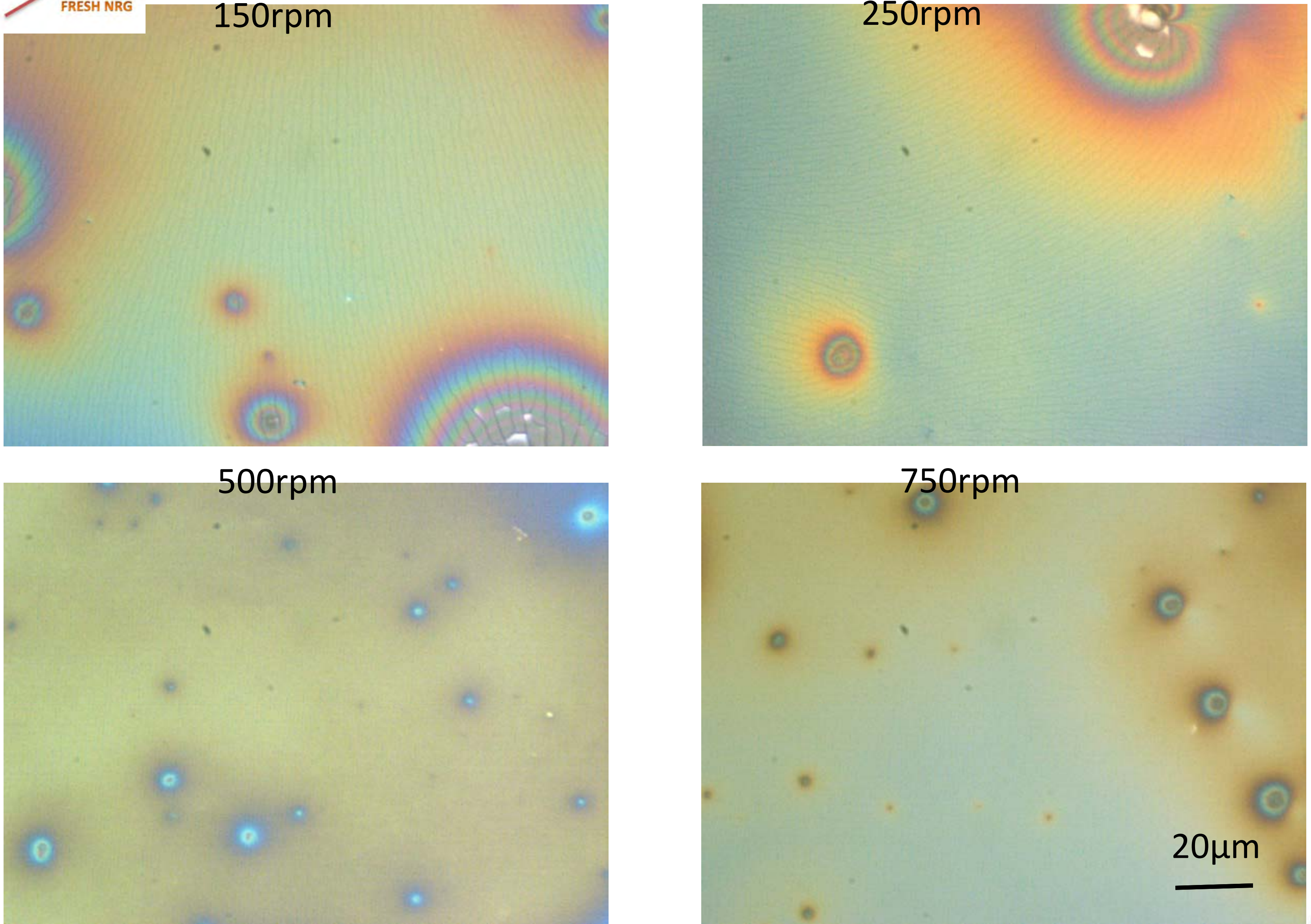
Factors affecting the control of the particle size:

- Cleanliness of glassware
- Water/moisture content of Reagents (age of reagent, anhydrous solvents)
- Silica:ammonia (Ratio) (linked to pH of the solution and water ratio)
- Temperature
- Aging

Experimental Observations Highlighting factors:

Description	Observation
Old bottle of TEOS used (TEOS2)	Milky sol formation due to particle growth in under 36hrs. SOL difficult to apply through 0.2micron syringe filter.
New bottle of TEOS used (TEOS3)	Sol still looks clear after 11 days.
Before Reflux of TEOS3	SOL applied through 0.2 micron syringe filter
After Reflux of TEOS3	SOL difficult to apply through 0.2micron syringe filter.

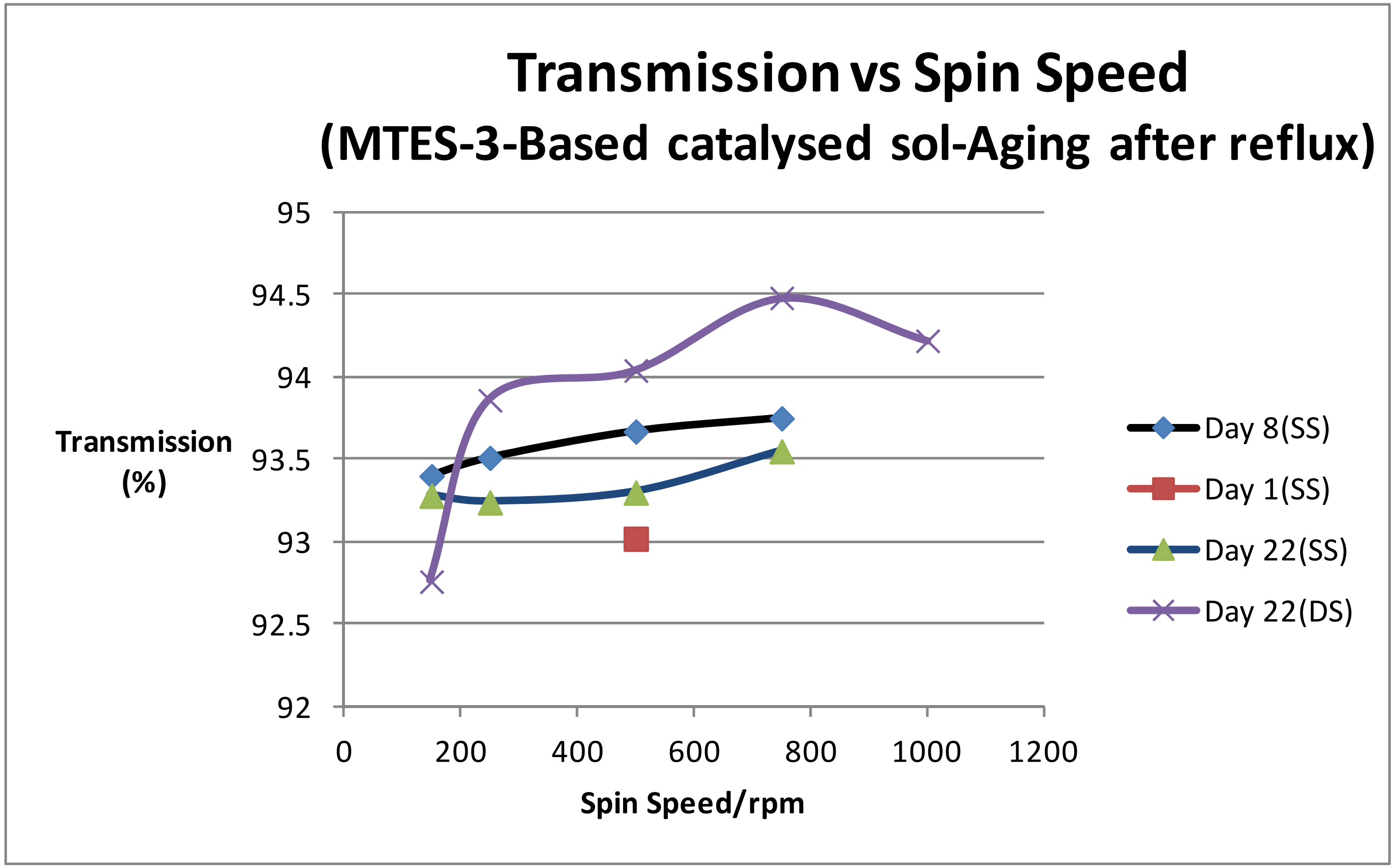
TEOS2 Films



Single side coated comparison for TEOS films made from two different Reagent Bottles

Process	Sample	Silica sol (type)	Spin speed (rpm)	Transmission	Reflection	Absorption
St. Clean	Si 105	TEOS-3(D6)	750	93.51	5.37	1.12
Plasma	Si 106	TEOS-3(D6)	750	93.60	5.38	1.02
Not filtered St. Clean	Si 109NF	TEOS-3	750	93.85	5.35	0.80
Not filtered St. Clean	Si 85	TEOS-2(D7)	500	91.28	5.26	3.46
	Glass			92.36	7.29	0.35

Necessary Aging study required for the Base Catalysed SOL Approach



Potential Sol Characterisation Technique

Particle Size Measurement: Zetasizer (Malvern Instruments)

SOL TEOS-3	Run1	Run2	Run3	Mean
After reflux Filtered	42.3	42.2	37.8	40.8
Not Refluxed	57.3	58.9	59.8	58.7

Note: Although the particle size is relatively large the measurements showed narrow distribution of particle size.
It may be possible to correlate a particle size to a subsequent good film transmission.

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Experimental Observations to Think about:

Base catalysed sols showed sedementation with time, but could be redispersed with swirling. ie should remain dispersed in a pumped system. (also reported in the literature)

The MTES base catalysed SOL could be filtered, but the TEOS could not, and the TEOS aging showed a more rapid nanoparticle suspension formation than the literature suggested. (This may relate to the TEOS reagent quality/deterioration.)

Even after reflux, aging of the SOL may be an issue.

A controlled reflux process removes the ammonia odour which should help in the tube coating environment.

Absorber Coating Sol Route

Alumina/Nickel based Coating:

Target was to produce a coating with dispersed Nickel nanoparticulates within an Alumina matrix.

Main Challenges:

- Achieve a stable suspension of the relatively dense Nickel particles within sol.
- Maintain metallic nature of Nickel within sol and after deposition.
- Achieve a high loading of Nickel within

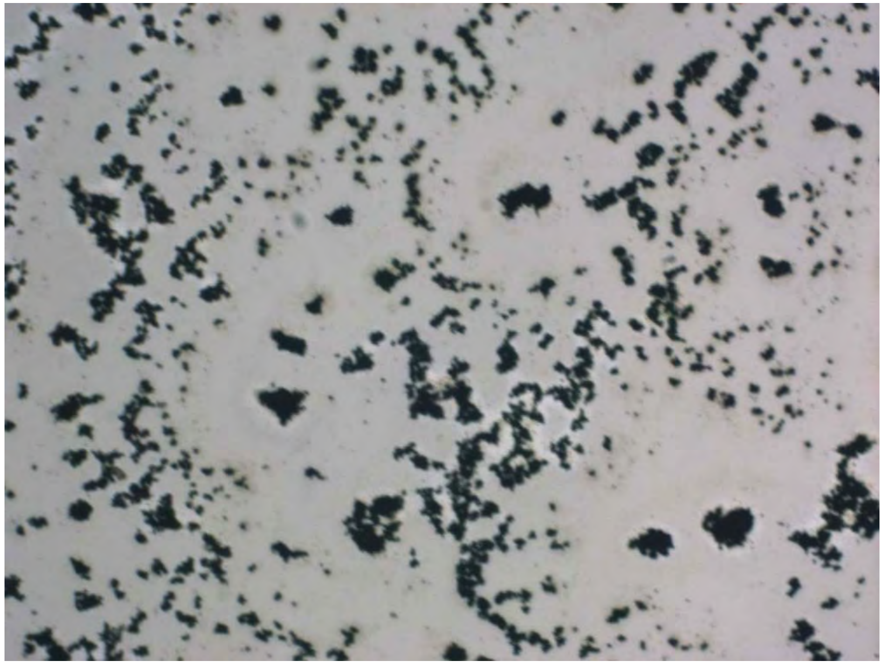
Initial Formulation:
Al(NO3)3.9H2O/PVA /Sodium Stearate/H20/NH4OH/Ni

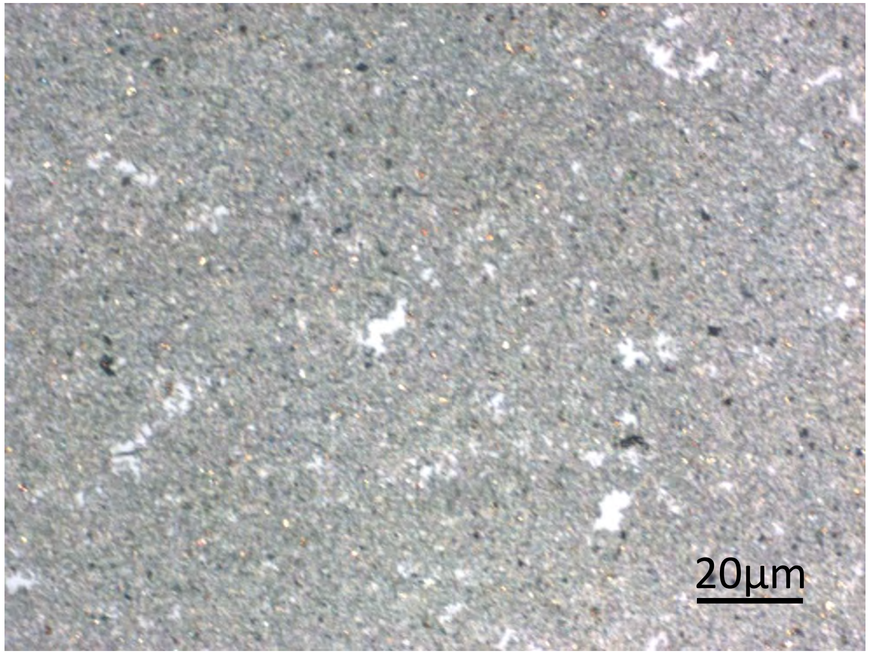
(0.11M Al-Ni component with 50/50 ratio of metals)

15 hour ball milling in pH>9 used to aid suspension of Ni.

Al-Ni-0.2 sample

Al-Ni-0.11 Sample –Ball milled –pH shifted





Achieved suspension of Ni particles by pH shifting, and ball milling, but the stability of the Aluminium Nitrate or PVA component doesn't seem to be good in this formulation, and wettability is an issue because of the high water based content at this point.

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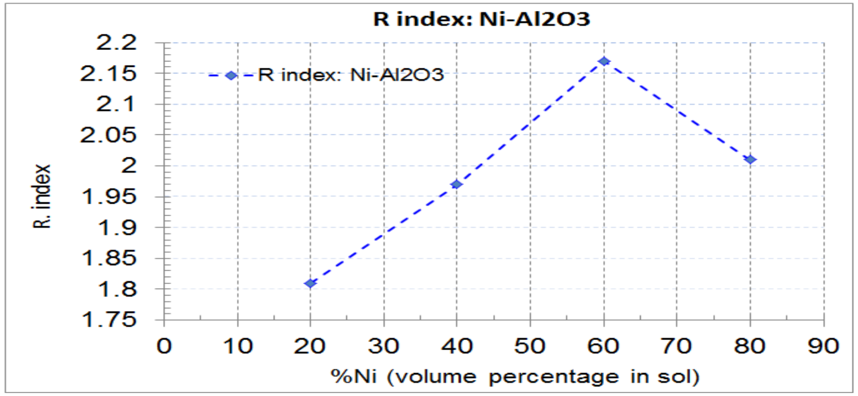
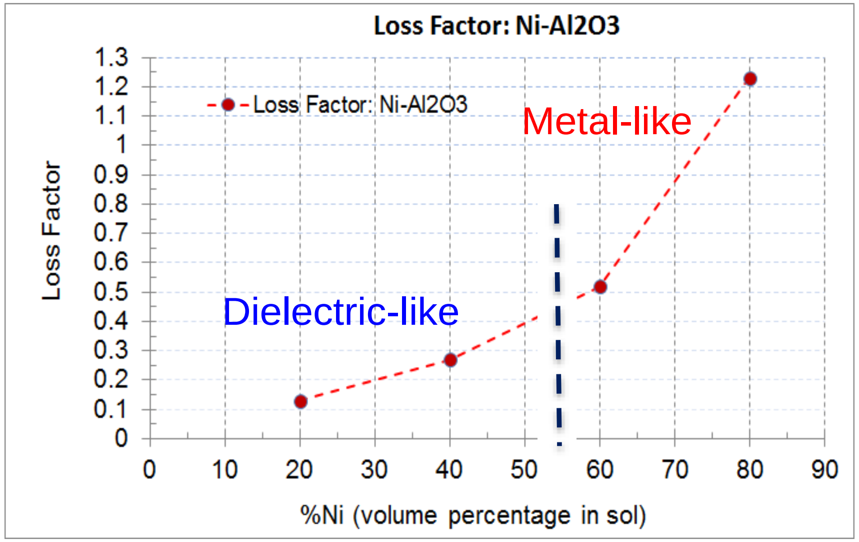
Design, development and deposition of an absorber coating using Ni-Al_2O_3 sol

Layer	Thickness (nm)	Absorptance	Thermal Emittance 25C	Thermal Emittance 250C
50%Ni-50%Al_2O_3	150	78.41	9.38	12.25
pSiO_2/50%Ni	90/150	85.27	9.6	12.94
pSiO_2/20%Ni/50%Ni	90/90/150	89.02	10.86	16.81
Stainless steel (n=1.95, k=9.85)				
50%Ni	150	77.88	7.91	10.27
pSiO_2/50%Ni	90/150	84.61	8.08	10.83
pSiO_2/20%Ni/50%Ni	90/90/150	88.47	9.08	14.18
Ni substrate (n=2.85,k=12.75)				

Absorber Coating using Ni-Al2O3 Sol



Variation of refractive index for a Ni-containing sol coating*



Variation of loss factor for a Ni-containing sol coating – there is a transition from dielectric-like to metal-like behaviour at around 55 vol %-Ni*.

**Bostrom et al. Solar Energy Materials & Solar Cells 91 (2007) 38–43*

Modified 3-layers Ni-Al2O3 Sol: Optimum Design

An ideal solution

Layer	Material	Complex Refractive index		Thickness (nm)	Absorptance	Emittance	
		Real	Loss factor			25C	250C
AR	$pSiO_2$	1.38	0	70	**94.93**	3.85	**7.03**
2nd layer	20-40%Ni-Al_2O_3			70			
1st layer	60-80%Ni-Al_2O_3	2.17					
Substrate		1.95	18.85				

f the sol characteristics of the 1st layer can be designed to have a loss factor of around 1.4, and the 2nd layer to have a loss factor around 0.31, the model predicts both high absorbtance and low emittance.

AIR SIDE

Thickness	Absorptance	Emittance	
		25C	250C
70/70/95	94.93	3.85	7.03
80/80/95	95.16	3.96	7.44

By varying thickness – absorbtance & emittance can be engineered

Alternative absorber coating materials VOx

- Offer the potential of high absorptance and low emittance
- VOx would seem the best system, where x= 2.0-2.5. Doping changes the transition temperatures up to 375oC for x=2.5. e.g. Nb, Mo, W, Ti, La, Mn, Cr are all possible although Ti and W are the most used.

- The low emissivity for a VOx based system would appear to be around 0.2-0.6 depending on the substrate(for us the absorber) temperature.

- Stability of VOx is desirable; e.g. can be achieved via a 2-layer system, VO_2/SiO_2 (provides environmental protection + stabilise oxygen content in coating).

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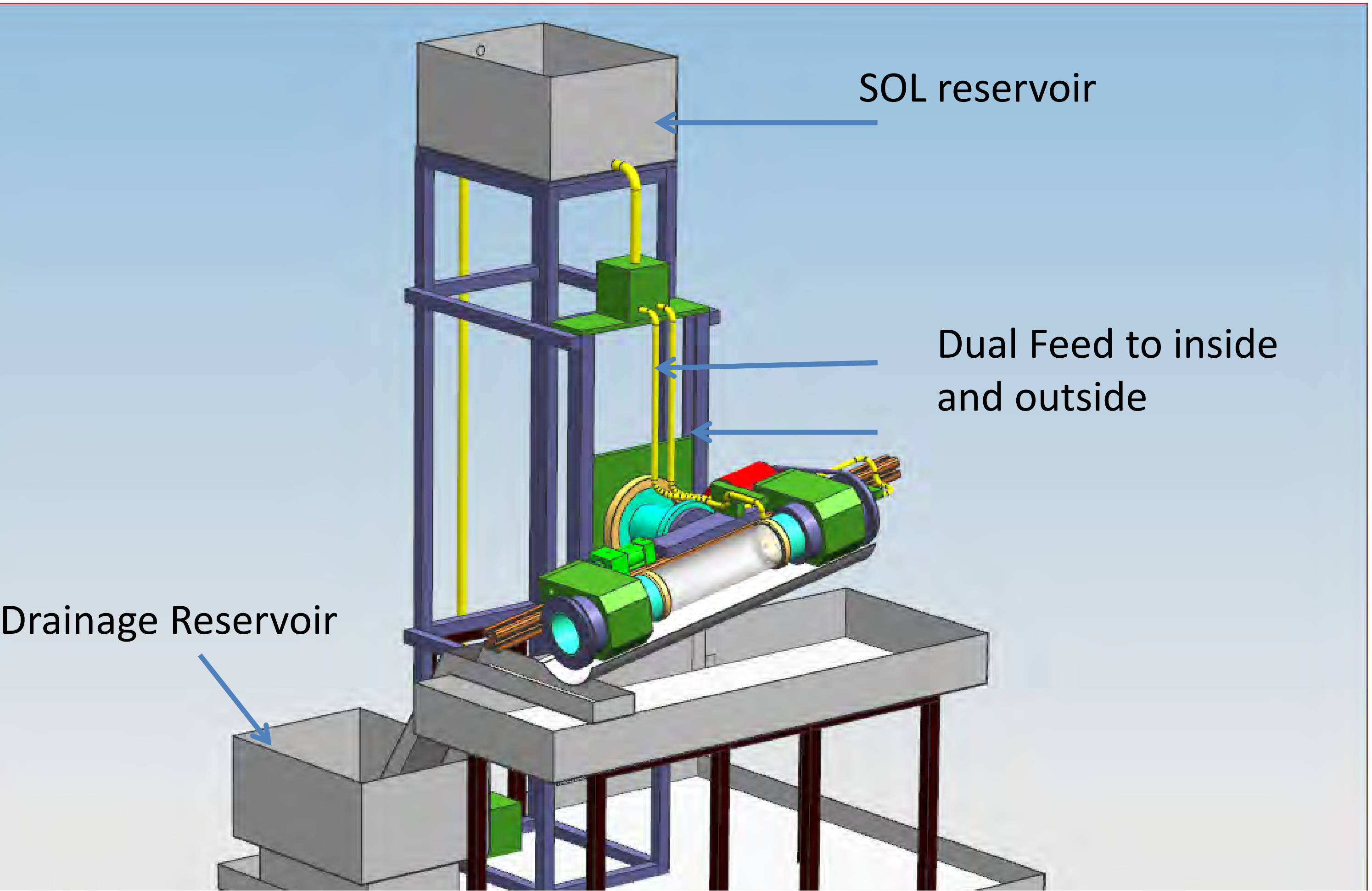
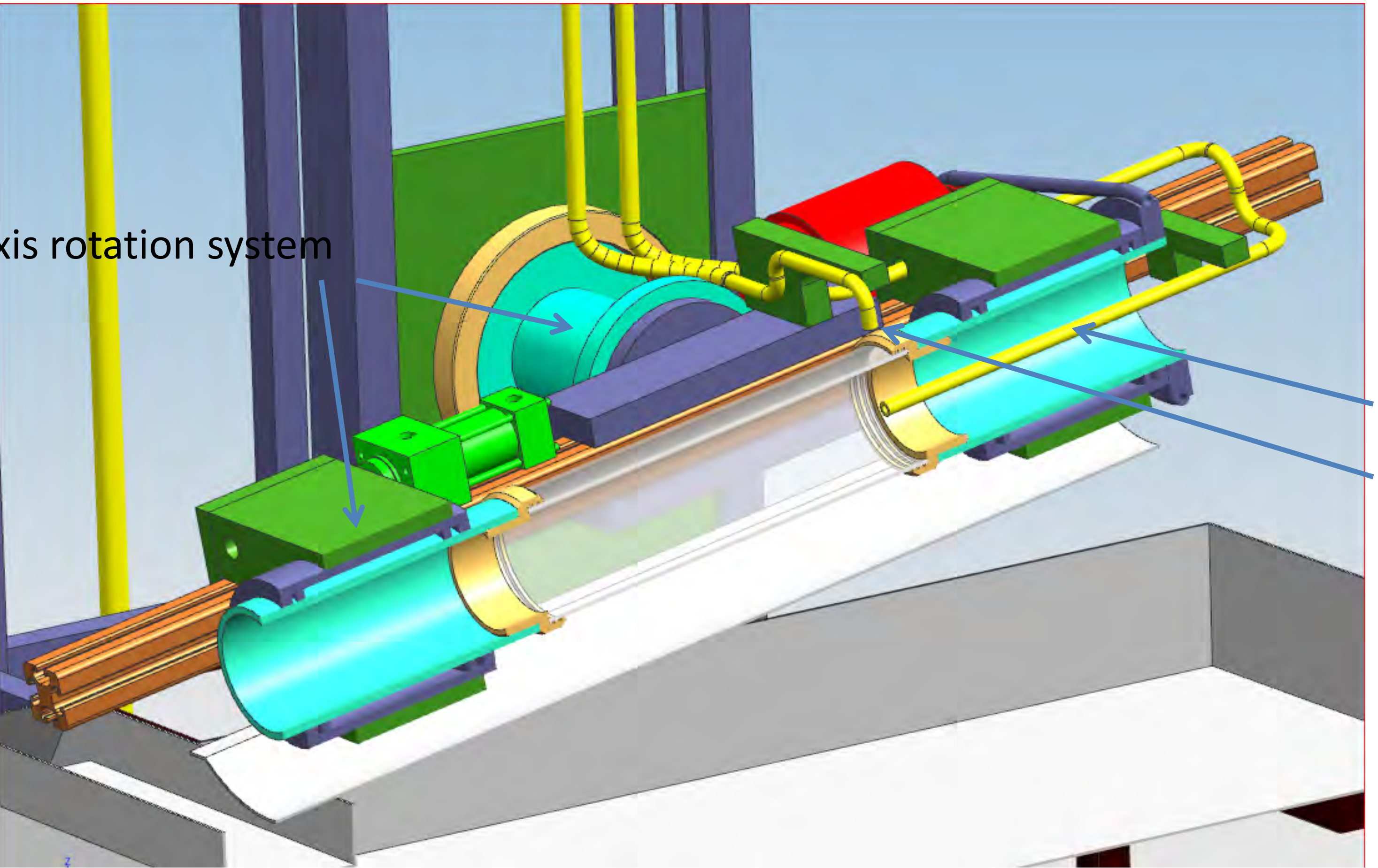
3-Layers Solar Absorber Coatings with VO2

Structure	R. Index	Thickness (nm)	Absorptance	Emittance (25C)	Emittance (250C)
MgO/ 20-30% Nickel-Al2O3/ VO2	1.38, 0	90/90/90	94.85	3.78	7.11
	1.81, 0.25	100/100/100	95.61	4.21	8.60
	2.55, 1.05	110/110/110	95.85	4.69	10.32
MgO/ 20-30% Nickel-Al2O3/ VO2	1.38, 0	90/90/90	94.97	4.12	8.18
	1.81, 0.25	100/100/100	95.43	4.62	9.98
	3.11, 1.05	110/110/110	95.48	5.21	12.08
SS	1.95, 18.85				

Tube Coater Schematic



Internal Section of Tube holder



Dual Feed

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tential benefits of coating design in the Development stage:

Handles Variable Tube lengths.
(for small test lengths)

Can operate either via a circulated SOL supply approach or application of measured volumes. (useful for test SOL volumes)

Variable rotation speed and tilt angle to determine parameters for SOL coating.

"Horizontal" design to enable coating of 4m tubes in a low roof facility.

Flexibility to coat one or both sides.

Some Challenges

sfer of optimised optical properties from spin coated flat substrates to
ting tube.

Simple dilution or may require new SOL formulation)

orm wetting of large glass tube area, and uniform drying.(requires good
ning/drying process of tubes prior to coating)

ding “guttering effects “ inside the tube.

g drying times

ability of the final coating.