

Hydrogen / Argon Plasma Cleaning of a Sub-3 nm Cobalt Thin Film: Native-Oxide and Hydrocarbon Removal Verified by Surface Contact Resistance

Instrument: Tergeo plasma cleaner (direct + downstream/remote modes)

Study basis: customer demonstration, 2018

1. Summary

This note documents a plasma-cleaning demonstration performed on a customer-supplied metal thin film: cobalt (Co) less than 3 nm thick carrying a native cobalt-oxide layer and adventitious hydrocarbon contamination. The objective was to remove the surface oxide and organic contamination without damaging the extremely thin metal film, and to confirm the effect through the improvement in surface contact resistance. Cleaning was carried out on the Tergeo plasma cleaner using pure argon, pure hydrogen, and argon/hydrogen mixtures, in both direct (immersion) and downstream (remote) modes. After plasma treatment the surface contact resistance became markedly more stable and measurably lower. PIE Scientific confirmed cleaning in real time with a two-point multimeter across opposite corners of each coupon; the customer then measured the returned coupons with a four-point probe. The customer's four-point-probe data showed sheet-resistance reductions of roughly 9–25% under effective conditions, with the largest reduction (25%) obtained using pure hydrogen plasma. The results confirm that the Tergeo system is effective for chemically reducing native oxide and removing hydrocarbon on delicate metal thin films while preserving film integrity.

2. Background and objective

A native oxide and adsorbed hydrocarbon layer on a metal surface increases contact resistance and degrades the electrical performance of thin-film devices. For a Co film under 3 nm, any cleaning process must be gentle: aggressive ion bombardment would sputter or damage the film. Hydrogen plasma is attractive because atomic hydrogen chemically reduces the metal oxide (e.g., $\text{CoO} / \text{Co}_3\text{O}_4 + \text{H} \rightarrow \text{Co} + \text{H}_2\text{O}$) and reacts with hydrocarbons to form volatile species, rather than relying on physical sputtering. Pure argon plasma cleaning relies physical ion surface sputtering to remove the native oxide and hydrocarbon contamination. Argon can be mixed with hydrogen to make the pressure more stable because it's hard for regular vacuum pumps to pump out high molecular speed hydrogen molecules.

The demonstration set out to answer three questions:

- Can the Tergeo system remove the native oxide and hydrocarbon from a sub-3 nm Co film?
- Which chemistry — pure Ar, pure H₂, or Ar/H₂ mixtures — and which mode (direct vs. remote) is effective?
- Does the treatment produce a measurable, repeatable improvement in surface contact resistance?

3. Experimental

3.1 Sample

Customer-supplied coupons, approximately 1×1 inch, each a Co thin film (< 3 nm) with native oxide and hydrocarbon contamination. Nominally identical coupons were used for all conditions.

3.2 Equipment and process control

- Tergeo plasma cleaner with 13.56 MHz RF power (0–150 W, adjustable in 1 W steps; continuous or pulsed operation, duty cycle 1/255 to 255/255).
- Integrated direct (immersion) and downstream (remote) cleaning modes, selected by recipe.
- Mass-flow-controller (MFC) regulated delivery of argon and hydrogen, allowing reproducible pure-gas and mixed-gas recipes; high-purity quartz chamber and sample holder to avoid metal contamination.
- Chamber pressure controlled through gas flow, in the range of roughly 0.15–1 Torr. For pure hydrogen a low flow was used to keep pressure stable; adding argon (≈ 10 sccm) further stabilized pressure and improved repeatability.

Note on flow units: gas flows are reported in sccm as indicated by the MFC. The MFC is calibrated for air, so the hydrogen values are consistent and repeatable but not absolute.

3.3 Metrology

Two independent resistance measurements were used. During processing, PIE Scientific used a two-point probe (hand-held multimeter, contacts at opposite corners of each coupon) to confirm cleaning in real time. The treated coupons were then sealed to limit re-oxidation and returned to the customer, who measured sheet resistance on a four-point probe. Both data sets are reported below: PIE's two-point readings (Section 4) give the in-process confirmation, and the customer's four-point-probe results (Table 1) provide the quantitative measure of the improvement.

4. Results

In PIE's in-process two-point check, the resistance before cleaning was highly unstable — readings ranged from a few hundred ohms to the kilo-ohm and even mega-ohm range, and the probe had to be moved to find a stable low reading. This behaviour is characteristic of a discontinuous, insulating native-oxide surface. **After plasma cleaning the reading became stable and consistently lower, dropping to roughly 70% of the lowest pre-clean value in the two-point check — a clear qualitative sign that the oxide/contamination barrier had been removed.**

The customer's four-point-probe results, measured on the returned coupons, are given in Table 1. Sheet resistance dropped under every effective condition, spanning pure argon, pure hydrogen, and Ar/H₂ mixtures, in both direct and remote modes. Customer's four-point-probe measurements were carried out five to six days after the samples were plasma cleaned in our facility. This could contribute to some surface degradation during the long delay.

Table 1. Plasma conditions and the customer's four-point-probe sheet-resistance results (measured on the returned coupons).

ID	Mode	Ar (sccm)	H ₂ (sccm)	RF (W)	Duty cycle	Time (min)	Rs before (Ω/sq)	Rs after (Ω/sq)	Reduction
A1	Direct	0	1	50	255/255	1	99.71	89.78	9.9%
A2	Direct	0	1	50	255/255	5	99.80	80.76	19.1%
A3	Direct	0	1	25	64/255	5	109.04	110.52	-1.4%
A4	Direct	0	1	150	255/255	5	109.91	82.04	25.4%
A5	Direct	20	10	150	255/255	4	98.30	88.95	9.5%
A6	Direct	10	3	50	255/255	6	98.97	87.10	12.0%
A7	Direct	0	1	50	255/255	2	98.90	81.96	17.1%
A8	Direct	10	0	50	255/255	2	98.19	82.04	16.4%
A9	Remote	10	3	100	255/255	4	99.17	87.62	11.7%
A10	Remote	0	1	100	255/255	2	97.79	88.92	9.1%

All coupons cut from nominally identical material. Row A3 (25 W, heavily pulsed 64/255) delivered too little energy to clean and is the only condition showing no reduction.

4.1 Key observations

- Best result — pure hydrogen: A4 (pure H₂, 150 W, direct, 5 min) gave the largest reduction, 25%, consistent with chemical reduction of the cobalt oxide by atomic hydrogen.
- Pure argon also works: A8 (pure Ar, 50 W, 2 min) reduced sheet resistance by 16%, showing that gentle physical cleaning plus removal of loosely bound contamination is effective on its own.
- Ar/H₂ mixtures and remote mode: mixed-gas and downstream/remote conditions (A5, A6, A9, A10) all produced reductions of ~9–12%, confirming a gentle, ion-reduced process still cleans the film.
- Power and time matter: higher RF power and longer exposure increased the reduction (compare A1/A7/A2 at 50 W with A4 at 150 W). The single non-performing case, A3, used only 25 W at a low 64/255 duty cycle — insufficient energy for effective cleaning.
- Process latitude: effective cleaning was achieved across a wide range of gas chemistries, modes, powers and times (typically 2–4 min at moderate power), indicating a robust, forgiving process window rather than a single narrow recipe.

4.2 Plasma appearance

Photographs of the running plasma over the sample confirmed a uniform, stable glow in both pure argon and pure hydrogen — important for even treatment of the film across the coupon.

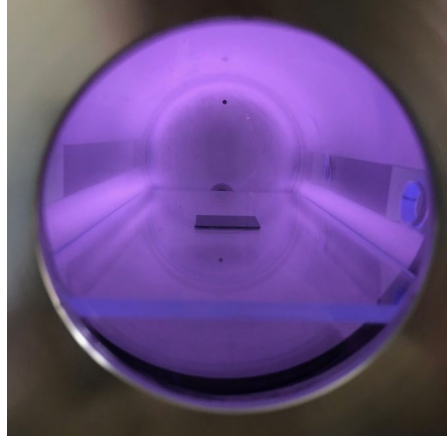


Figure 1. Argon plasma over the Co coupon — uniform violet glow.

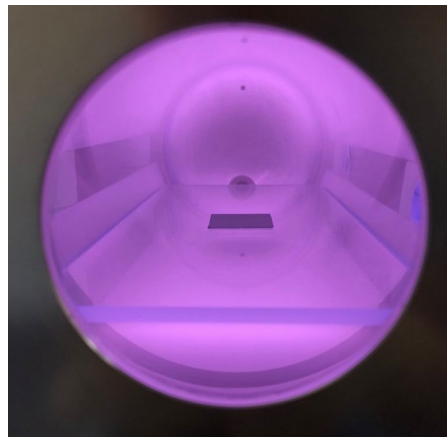


Figure 2. Hydrogen plasma over the Co coupon — uniform magenta glow.

4.3 Measurement timing and re-oxidation

An important caveat applies to the four-point-probe results. The Round A coupons were plasma-cleaned at PIE on approximately 25 July 2018, shipped the following day, received by the customer on 27 July, and the four-point-probe results were reported on 31 July. The measurement was therefore taken roughly five to six days after plasma cleaning, with shipping and an intervening weekend; the exact probe date was not recorded. A sub-3 nm cobalt surface re-oxidizes and re-adsorbs hydrocarbon rapidly on exposure to air. The coupons were sealed to limit this, but they were not measured in a controlled inert environment, so partial re-oxidation during the delay is expected.

Because re-oxidation raises the measured sheet resistance, the customer's reductions (9-25%) should be read as a conservative lower bound: the true improvement immediately after cleaning was almost certainly larger than the delayed measurement indicates. This is consistent with PIE's in-process two-point check, taken immediately after cleaning, which showed a larger relative drop (roughly 400 to 270 ohm, about 30%) than most of the delayed four-point-probe values. In other words, the difference between PIE's larger apparent improvement and the customer's smaller four-point-probe improvement is well explained by the several-day delay and air exposure between cleaning and measurement, not by a discrepancy in the cleaning itself.

For the subsequent Round B coupons, PIE explicitly requested same-day measurement to minimize recontamination, and the customer measured them on the day of receipt (about a two-day delay) - a better-controlled comparison and a practice recommended for any future evaluation of freshly cleaned metal surfaces.

5. Discussion

The combination of a large, unstable pre-clean resistance and a stable, lower post-clean resistance is the signature of removing an insulating native-oxide / hydrocarbon layer from a metal surface. Two mechanisms act together on the Tergeo system: atomic hydrogen chemically reduces the cobalt oxide and volatilizes hydrocarbons, while argon provides gentle physical cleaning; the downstream/remote mode delivers these reactive species with minimal ion energy, protecting the sub-3 nm film. Because the 13.56 MHz source generates a dense plasma at low RF power, effective cleaning was obtained at only 50–150 W and short cycle times, avoiding the high powers and ion damage associated with low-frequency (kHz) systems. The quartz chamber and sample holder further ensure the cleaning does not introduce metal contamination onto the sensitive surface.

6. Conclusion

The Tergeo plasma cleaner effectively removes native oxide and hydrocarbon contamination from a sub-3 nm cobalt thin film, as demonstrated by a stable and measurable reduction in surface contact resistance. Effective cleaning was achieved with pure argon, pure hydrogen, and argon/hydrogen mixtures, in both direct and downstream/remote modes, across a wide process window. In the customer's four-point-probe measurements, sheet resistance was reduced by up to 25% under the best (pure-hydrogen) condition, with pure argon and mixed-gas conditions delivering 9–16% reductions. These results confirm the Tergeo system as an effective, gentle, and repeatable tool for surface preparation of delicate metal thin films where low contact resistance is required.