Suppressed Hysteretic Field Emission from Polymer Encapsulated Silver Nanowires

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Abstract—Suppression of the hysteretic electron emission in one-dimensional nanomaterial-based electron sources remains a critical barrier preventing their wide scale adoption in various vacuum electronics applications. Here we report on the suppressed hysteretic performance, and its photo-dependence from conformal poly-vinylpyrrolidone (PVP) encapsulated percolative Ag nanowire (NW)-based electron sources.

Index Terms—silver nanowires, field electron emission, adlayer, hysteresis, poly-vinylpyrrolidone

I. INTRODUCTION

The field of vacuum electronics is undergoing a renaissance. With significant interest in the application of field electron emission in flat panel displays, parallel electron beam lithography systems, space propulsion, chemical analysis, microwave amplifiers, lighting, and X-ray sources[1-5], the integration and rational synthesis of nanoscale systems is allowing otherwise challenging emission geometries to be realized via near atomic-scale self-assembly. Nanomaterials are continuing to find ever more varied and diverse applications in the field of vacuum electronics. Though many proposed ideas are technologically unfeasible, the use of the myriad nanowire (NW) types in electron emission devices has significant potential, principally due to their intrinsically high aspect ratios[6, 7]. Nevertheless, such systems remain plagued by hysteresis within their electron emission, which significantly degrades the cycle-to-cycle reproducibility of the transport. Various suggestions have been put forth as to the source of such hysteresis within nanoscale electron emission systems, including; back-bombardment from desorbed ionized species[8] and subsequent micro-plasma mediated morphological deformation, emission from transient intermediate energy states[9], dynamic bias ramp-rate effects, transient emitter field-dependent electrostatic alignment[10], deep level carrier capture, oxide charging, and trap de-population[11]. Others have attributed such hysteresis effects to both reversible[12] and irreversible structural changes[13] in the emitters. The detailed underpinning mechanism remains largely unclear, though it likely stems collectively from many of these sources. Though certainly not all, most mechanisms proposed relate to the fine physiochemistry of the emitters surface. Emitter encapsulation has been shown elsewhere to enhance the temporal stability of various one-dimensional nanoscale electron sources [14, 15], with various polymer adlayers[16-20] evidencing potential as emission enhancing and hysteresis suppressing over-coatings. Here, via broadband optical excitation, we investigate the hysteretic field emission performance of percolative networks of poly-vinylpyrrolidone (PVP) encapsulated Ag NWs.

II. RESULTS & DISCUSSION

Figure 1 illustrates the electron source fabrication procedure. All chemicals were purchased from Sigma-Aldrich and were used without further purification. Ag NWs were synthesized according to our previously reported method[21]; 10 mL, 0.45M EG solution of PVP (MW = 55000, [C\textsubscript{6}H\textsubscript{4}NO\textsubscript{2}]\textsubscript{5}) was prepared with 7 mg NaCl (99.5%). The solution was heated to 170°C in...
a 100 mL bulb and a 0.12M AgNO₃ (99.5%) solution in 5 mL of EG (C₆H₁₂O₂) was prepared and added, dropwise, into the PVP solution by injection pumping (Top-5300 syringe pump) at a rate of 5 mL/h. The solution was magnetically stirred at 1000 rpm throughout. All solutions were kept for a further 30 min at 170°C and were subsequently air-cooled to room temperature. The as-synthesized Ag NW solution was purified using diluted acetone (1:5) with double centrifugation at 8000 rpm for 20 min. NWs were then dispersed in ethanol and again centrifuged at 8000 rpm for an additional 20 min. The final product was dispersed in ethanol for further characterization and processing. To fabricate the electron sources, ethanolic-suspended Ag NWs were deposited onto 200 nm thermally oxidised p-doped silicon substrates by nitrogen driven spray coating, with the substrates heated to 120°C on a hot plate. Samples were 10x10 mm with a controlled Ag NW coated area of 9x9 mm. For consistency, a single batch of Ag NWs was used to fabricate all samples investigated in this study. To assess the hysteresis effects of the PVP adlayer it was removed by further annealing at 200°C, for 20 mins in air, with the emission characteristics assessed thereafter.

Ag NWs had a mean diameter of 77.5±9.2 nm and a mean length of 7.32±0.41 μm (Figure 2(a)). Encapsulated samples had a mean PVP thickness of 2.9±0.5 nm. A typical scanning electron micrograph of a fabricated emitter is show in Figure 2(b) which has a typical areal NW density of 0.143 (±0.009) mm² (Carl Zeiss Gemini 50 scanning electron microscope, 20 kV). Spray coating resulted in no preferential alignment of the NWs. Ag NW densities exceeded the percolation threshold in all cases. The inset in Figure 2(b) depicts a typical fabricated emitter. Electron micrographs were analysed using the particle analysis tool kit in the freeware, ImageJ. As shown in Figure 2(c), HR-TEM micrographs (FEI Tecnai F20 TEM) suggest the formation of a surface oxide of thickness of around 1 nm, with XRD spectral peaks at 38° and 44° corresponding to the (111) and (200) Ag planes (JCPDS card 04-0783) (Figure 2(d)). Though challenging to assess, the PVP has likely adopted its atactic configuration, with the resulting layer functioning principally as a thin diffusion barrier. HR-TEM reveals that the conformal PVP coating hermetically seals the Ag NWs, largely inhibiting further deleterious trap-forming surface oxidation at STP, though not prior to the unavoidable growth of a native surface oxide during synthesis. Acquired on Csl substrates, FT-IR spectroscopy (Thermo Fischer) revealed that annealing at > 300°C removed all NWs which defined our viable PVP-removed annealing temperature window, with quenching of the C-C (830 cm⁻¹), C-N (1230 cm⁻¹), CH₃ (1448 cm⁻¹), and the broad O-H stretching (3184-3568 cm⁻¹) modes suggesting removal of the PVP for temperatures > 200°C. XPS and cross-sectional EDX mapping (LEO 1530 VP GEMINI SEM, 15 kV, Oxford Instruments 7426 detector) showed some (<5%) Au, Cr, Co, and Fe contamination, whilst also highlighting the clearly conformal PVP coating. Scanning electron microscopy and Raman spectroscopy (Renishaw InVia, scanned in triplicate, 515 nm, x50 aperture, incident < 5 mW) of the coated and uncoated samples indicate that though much of the PVP is removed during thermal annealing some agglomerates remain. The enhanced Raman peak at 1573 cm⁻¹ has been assigned elsewhere to the C=O stretching mode, indicating that much of the PVP interaction with the underlying Ag NW is mediated through the oxygen lmbj22]. Similarly, the enhancement of the 2937 cm⁻¹ asymmetric stretch suggests this CH₃ chain is in proximal contact with the Ag NW surface223, highlighting the PVPs central role in acutely adjusting the surface barrier and hence its critical role in augmenting the electron emission performance given the processes high surface sensitivity.

The PVP adlayer did not dramatically affect the macroscale sheet resistance. Any increase in the inter-NW contact resistance due to the PVP adlayer was largely negligible in that the barrier was sufficiently thin so as to not preclude significant tunnelling between adjacent NWs.

In the present paper, the photo-dependent hysteretic field electron emission performance was extracted from cyclic 1-E measurements. As depicted in Figure 3(a), field electron emission studies were conducted in a custom built ultra-high vacuum, turbo molecular pumped to 10⁻⁶ mbar. The Ag NW samples were grounded and a phosphor coated ITO/glass anode was mounted adjacent to the samples which was positively biased using a computer controlled variable high voltage supply (0-5 kV). Contacts were formed using silver dag. The inter-electrode vacuum gap was fixed and a constant circular emission area of 0.39 cm² was used, defined by a 500 μm thick mica restrainer. Measurements were conducted in diode mode with voltage increments of 20-100 V. Each current point was averaged from three separate measurements, following a 3s settling time. Currents were measured using a GPIB interfaced HP 34401A digital ammeter with 6.5-digit precision, independently verified using an array of conventional

![Fig. 2.](Image 55x470 to 289x735)
USB interfaced long working distance microscope equipped with a x200 objective.

For X-ray diffraction a Rigaku D/Max-2000 pc diffractometer, fitted with a Cu Ka source and operated at 40 kV, was used. For X-ray photoelectron spectroscopy a 120 electron energy analyser at room temperature and a MgKα,1.2 (1253.6 eV) X-ray source was used, obtaining an overall energy resolution of 0.8 eV. Following annealing, XPS showed a shift of 0.13-0.30 eV in the Ag 3d_{5/2} peak, attributed to augmented charge transfer between the Ag NW body and associated adlayers, confirming our thesis that extended annealing effectively removes the PVP adlayer[25], as further verified by in-situ RGA atmospheric analysis during annealing. UPS measurements were acquired using a He II radiation source (hv = 40.8 eV) with an energy resolution of 0.2 eV. UPS suggested that the work function of the nascent Ag NWs deleteriously increased from 3.37 eV to 3.70 eV for the PVP coated Ag NWs. Though suppressing emission hysteresis, assuming Fowler-Nordheim-like emission, the validity of which remains questionable at the nanoscale, such an increase in WF would deleteriously reduce the beam current. Indeed, our field emission measurements showed a ten-fold decrease in the maximum measured emission current (at 10 V/μm) upon PVP coating. Similarly, PVP coating deleteriously increased the turn-on field by approximately 1 V/μm. In Figure 3(b) banding is indicative of hysteretic emission. Though degrading the turn-on, we nonetheless find that the PVP adlayer supressed hysteretic emission substantially relative to the uncoated Ag NWs, particularly in the high field regime. Our preliminary monochromatic optical excitation studies show an evident hysteresis dependence on excitation wavelength. We attribute this to the formation of a stable interface between the PVP adlayer and the Ag NW. These sealed interfaces likely give rise to less variation, as a function of time, temperature and vacuum conditions, as compared to uncoated Ag NW emission sites. During emission, this passivated interface presents a more robust platform to thermally stimulated changes in the local vacuum environment, as well as local trap population. Further monochromatic wavelength dependent studies will be reported elsewhere.

Figure 3(c) shows the mean and standard deviation (1σ) I-E curves for a PVP coated sample, over 40 cycles, for dark and broadband illuminated conditions. There was a noticeable enhancement in the emission current with illumination, with an increase in emission current of approximately 140% at 10 V/μm. This is likely an effect of carrier excitation either in the PVP layer or PVP-Ag NW interface. This effect is non-bolometric; no noticeable increase in sample temperature was recorded. In Figure 3(b), odd cycle identifiers represent the field inclination, and even cycle identifiers represent the field declination. The observed electron emission is wholly associated with the Ag NW and Ag NW/PVP dispersions; control studies from uncoated Si and Si/SiO₂ substrates showed emission currents of < 10⁻⁹ A for electric fields up to 9 V/μm. PVP/Ag NW samples showed robust and repeatable emission across a wide range of base pressures (10⁻⁸–10⁻³ mbar). The DC temporal stability (24 hrs, 9 V/μm) of the PVP/Ag NWs was 22.6%, which deleteriously increased to 29.0% under broadband optical excitation. Conversely, a corresponding Gaussian distributed mean emission current during hysteresis data.
assessment of 0.27 (±0.24) µA (dark) and 0.44 (±0.14) µA (broadband optical excitation) was noted. During hysteretic measurements for the PVP coated samples it appears that optical excitation increased the absolute magnitude of the emission current but reduced the variability in the emission current. Interestingly, following a conditioning phase (which tended to increase the turn-on field with cycle number) the hysteretic performance of the PVP/Ag NWs in dark conditions was largely stable with cycle number, however, when broadband illuminated, the turn-on field tends to near-monotonically decrease with cycle number at a low rate of -0.04 \( \text{V/mm} \) 'cycle'\(^{-1}\). Hysteresis was increased by around 50% in the cycle studies upon optical excitation of the PVP coated samples though PVP coating showed, for both dark and illuminated conditions, a clear hysteresis suppression relative to the uncoated Ag NW samples.

III. CONCLUSIONS

In this communication we present our findings on the photo-dependent hysteresis and its suppression in field electron emission from Ag NW electron sources following coating with PVP. Compared to the uncoated Ag NW samples we find a near stable variation in turn-on field with cycle number for our PVP coated samples making the need for emission current feedback control and emitter conditioning redundant in such surface passivated nanoscale systems.

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REFERENCES

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