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STEM Degrees: 1 **STEM Participants:** 1

Major Goals: 1. Investigate the structural and SWIR (1700 nm – 2500 nm) optical properties of ultrathin transition metal alloy films deposited on silicon.
The PI hypothesizes that AuxPd1-x and CuxTi1-x will form disordered alloys with broadband absorption in the SWIR range. This is based on prior experimental work and first-principles simulations. The PI will use grazing incidence x-ray diffraction to verify the structural properties and spectroscopic ellipsometry to collect the complex permittivity of the alloy thin films over a broad range of stoichiometries.

2. Fabricate Alloy/Si Schottky diode photodetectors.
The PI hypothesizes that 10 nm flat films of CuxTi1-x or AuxPd1-x coupled with a SiO2/Al optical cavity will absorb ~90% of the SWIR light in the ultrathin metal absorbers. This is supported by preliminary electromagnetic simulations.

3. Characterize the alloy photodetectors responsivity and rise time.
The PI hypothesizes that the performance of the photodetector will not be limited by the RC time constant due to the ultrathin (e.g., 10 nm) absorber layer.

Accomplishments: ### Materials Deposition ###
- The PI developed a magnetron co-sputtering method for the deposition of CuPd and AuPd films under kinetic control. Co-sputtering offers significant advantages over the previous co-evaporation method used by the PI. As compared to evaporation, sputtering provides higher deposition rates and more control over the stoichiometry. Furthermore, the phase diagram for CuPd shows several regions where the two materials are not miscible. The rapid deposition rates offered by co-sputtering allows us to operate in a kinetically controlled regime and maintain miscibility and thus true alloy formation. We demonstrate single phase CuPd alloy formation in ultrathin films (<50 nm) in our publication (https://doi.org/10.1063/5.0102066) through grazing incidence x-ray diffraction.

Optical Properties
- We measured the ultrafast electron dynamics of CuxPd1-x films (5 nm thick) with 1550 nm pump excitation and mid-infrared and terahertz probe light. Both MIR and THz probe regions showed that dilute Pd alloys (i.e., sub 50 at% Pd) have longer hot carrier lifetimes than pure Pd films and generate more hot carriers than pure Cu. We also found that dilute Pd alloys did not exhibit the typical thermalization response found in our previously studied AuxPd1-x alloys. In short, CuPd alloys with dilute Pd composition showed negligible thermalization within 1 - 2 ps after the pump excitation. We hypothesize that this is due to photoluminescence. We are in the process of verifying

this with a collaborator in Japan.

Device Development
- Initial Schottky type photodetector devices were fabricated using p-type silicon as the hole acceptor and a thin alloy film as the photo absorber and hot carrier generator. Unfortunately, we were unable to measure responsivity from the devices with 1550 nm excitation. We suspect the issue is due to the design of the contacts, but there could also be issue with the hot-holes being reflected off the alloy/Si interface due to a mismatch in the momentum. Dark IV curves showed significant series resistance in the device. More work needs to be done to optimize the contacts and the device geometry before we can begin to address the momentum matching issue, which is a known issue in hot-carrier type photodetector devices.

Training Opportunities: Henry Cain, an LSU physics undergraduate, wrote his honors thesis on this project. Prior to starting the project Henry had never worked in a cleanroom. Henry learned the following techniques during his time on this project:

- Physical vapor deposition of metals
- Metal-Semiconductor electrical characterization via IV curves
- Direct write photolithography
- Annealing of semiconductor contacts

Upon graduation Henry was given an offer by Dow Chemical to work in their cleanroom in Delaware. Henry is currently still employed with Dow but pursueing a Dow sponsored Ph.D. in Physics at U. Penn. Henry is still working in the area of nanofabrication.

Results Dissemination: We published our findings on the emergent properties of CuPd alloy films under near-infrared excitation in The Journal of Chemical Physics, https://doi.org/10.1063/5.0102066

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PARTICIPANTS:

Participant Type: Undergraduate Student
Participant: Henry Cain
Person Months Worked: 9.00 **Funding Support:**
Project Contribution:
National Academy Member: N

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Participant Type: Staff Scientist (doctoral level)
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Abstract: Noble-transition metal alloys offer emergent optical and electronic properties for near-infrared (NIR) optoelectronic devices. We investigate the optical and electronic properties of CuxPd1?x alloy thin films and their ultrafast electron dynamics under NIR excitation. Ultraviolet photoelectron spectroscopy measurements supported by density functional theory calculations show strong d-band hybridization between the Cu 3d and Pd 4d bands. These hybridization effects result in emergent optical properties, most apparent in the dilute Pd case. Time-resolved terahertz spectroscopy with NIR (e.g., 1550 nm) excitation displays composition-tunable electron dynamics. We posit that the negative peak in the normalized increment of transmissivity (?T/T) below 2 ps from dilute Pd alloys is due to non-thermalized hot-carrier generation.
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Partners

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I certify that the information in the report is complete and accurate:
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Abstract

Noble-transition metal alloys offer emergent optical and electronic properties for near-infrared (NIR) optoelectronic devices. We investigate the optical, structural and electronic properties of Cu_xPd_{1-x} alloy thin films and their ultrafast electron dynamics under NIR excitation[1]. Ultraviolet photoelectron spectroscopy measurements show strong *d*-band hybridization between the Cu 3*d* and Pd 4*d* bands. These hybridization effects result in emergent optical properties, most apparent in the dilute Pd case. Time-resolved terahertz spectroscopy with NIR (e.g., 1550 nm) excitation displays composition-tunable electron dynamics. We posit that the negative peak in the normalized increment of transmissivity (ΔT/T) below 2 ps from dilute Pd alloys is due to non-thermalized hot-carrier generation. On the other hand, Pd-rich alloys exhibit an increase in ΔT/T due to thermalization effects upon ultrafast NIR photoexcitation. Cu_xPd_{1-x} alloys in the dilute Pd regime may be a promising material for future ultrafast NIR optoelectronic devices.

Objectives

1. Investigate the structural and SWIR (1700 nm – 2500 nm) optical and electronic properties of ultrathin transition metal alloy films deposited on silicon.

2. Fabricate Alloy/Si Schottky diode photodetectors.

3. Characterize the alloy photodetectors responsivity and rise time.

Findings

1. Investigate the structural and SWIR (1700 nm – 2500 nm) optical and electronic properties of ultrathin transition metal alloy films deposited on silicon.

The PI developed a magnetron co-sputtering method for depositing Cu_xPd_{1-x} alloy films under kinetic control. Co-sputtering offers significant advantages over the previous co-evaporation method used by the PI[2]. Unlike evaporation, sputtering provides higher deposition rates and more control over the stoichiometry of the alloy. Furthermore, the thermodynamically governed phase diagram for Cu_xPd_{1-x} shows several regions where Cu and Pd are not miscible. The rapid deposition rates offered by co-sputtering allow us to operate in a kinetically controlled regime and maintain miscibility and form a true alloy.

<u>Optical Properties</u>

A Woollam RC2 variable-angle spectroscopic ellipsometer was used to measure the Ψ and Δ values for optically thick 50 nm pure Cu, Pd, and Cu_xPd_{1-x} alloy films. Ψ and Δ values were collected over a 210–2500 nm wavelength range with 60°, 65°, and 70° incidence angles. The complex permittivity was determined for Cu, Pd, and the alloys by fitting the data to a two-layer (air-metal) Kramers–Kronig valid B-splines model using the CompleteEASE software package.

Figure 1a shows the real (ε_1) and imaginary (ε_2) permittivity values for sputtered 50 nm Cu_xPd_{1-x} alloy films and their constituent pure metals on silicon chips using spectroscopic ellipsometry spanning the ultraviolet to NIR wavelengths. Interband and intraband transitions in metal films strongly dictate the imaginary permittivity, i.e., dielectric losses. As shown, Cu exhibits the lowest losses of all the films in the NIR because the excitation energy is below the interband energy threshold (IET) for Cu, which is ~2.1 eV (~590 nm). Pd, on the other hand, has interband transitions close to the Fermi level and thus exhibits significantly higher losses since both interband and intraband transitions are accessible in the NIR. The inset in **Figure 1(b)** shows the trend in the ε_1 and ε_2 permittivity at 1550 nm (dashed line) as an increasing fraction of Pd is added to the alloy films. As Pd is added to the alloys, the ε_1 and ε_2 values increase, with most of the change in the permittivity values occurring before 50 at. % Pd fraction is reached. Beyond 50 at. % Pd, the real and imaginary permittivity trend flips, with both values decreasing slightly as pure Pd approaches. These results clearly show that the optical properties of the Cu_xPd_{1-x} alloys are not simple ratios of the pure films. Our previous study of Au_xPd_{1-x} alloy films[2] also observed non-simple mixing of the pure optical properties, but Cu_xPd_{1-x} films show even more non-linear behavior indicative of stronger hybridization effects, as we initially predicted.

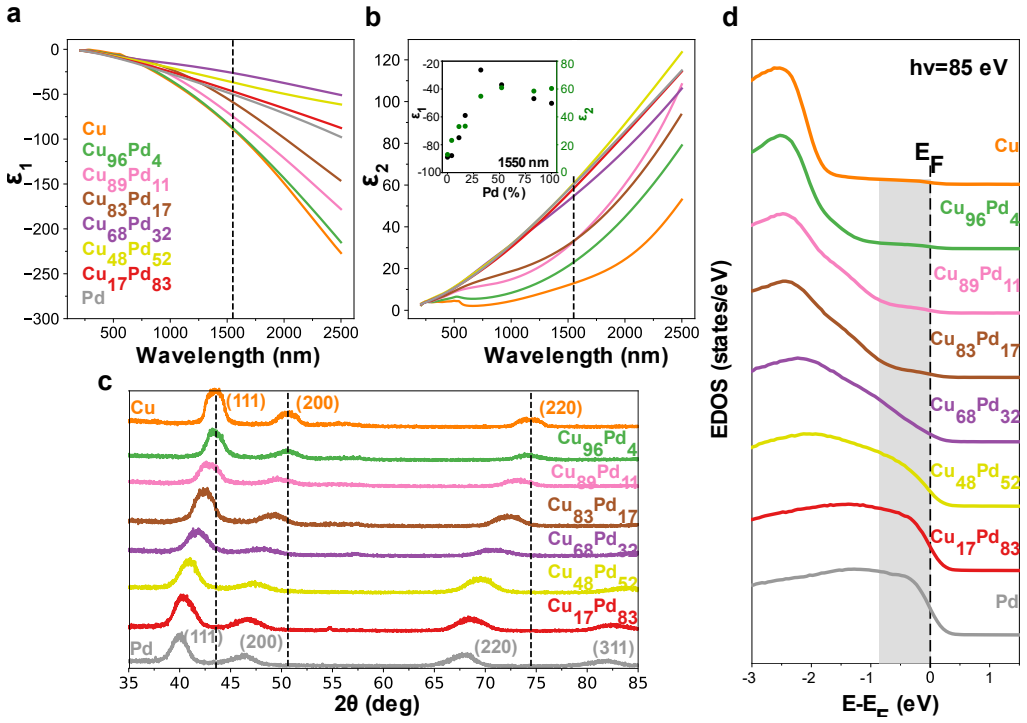

Figure 1. Optical, structural, and electronic properties of Cu, Pd, and Cu_xPd_{1-x} alloy films. (a) Real and (b) imaginary permittivity measured by spectroscopic ellipsometry (inset) ε_1 and ε_2 at 1550 nm as a function of alloy composition. (c) Grazing incidence x-diffraction patterns showing that the Cu_xPd_{1-x} alloy is a homogeneous fcc phase and (d) EDOS measured by ultraviolet photoelectron spectroscopy. Increasing the Pd fraction shifts the EDOS toward the Fermi energy (E_F). The gray box below E_F signifies the region of the EDOS we are exciting with the NIR pump studies in Figure 2.

Structural Properties

A PANalytical EMPYREAN x-ray diffraction (XRD) with a Chi Phi XYZ 5-axis cradle stage equipped with Cu Kα radiation was used to evaluate the phase composition of the films. The samples were pre-aligned at maximum Si(100) intensity, and the scans were performed at a 0.5° incidence angle omega.

Unlike the Au–Pd system, which is miscible for all compositions in the solid phase, the Cu–Pd thermodynamic phase diagram exhibits several regions of immiscibility at room temperature. To avoid phase segregation in our Cu_xPd_{1-x} films, we sputtered them at high rates to lock in a single-phase structure. To verify the phase behavior of the Cu_xPd_{1-x} films, we used grazing incidence x-ray diffraction (GIXRD). The GIXRD patterns in **Figure 1(c)** confirm that our thin-film Cu_xPd_{1-x} alloys are single-phase alloys. Figure 1(c) also shows that all samples are polycrystalline FCC, and from top to bottom, we see how the Bragg peaks shift to larger spacings as we add the larger Pd atom into the Cu lattice. As predicted by Vegard's law, the lattice constants of the alloys falls between the lattice constant of the pure metals with some deviation from linearity.

Electronic Properties

We acquired synchrotron-based ultraviolet photoemission spectroscopy (UPS) data from the thin films to better understand the electronic structure changes upon alloying pure Cu and Pd metals. In addition to examining the valence states of the alloys, we used x-ray photoelectron spectroscopy (XPS) to investigate subsequent changes in the core levels of each of these metals to probe their chemical states. Because these two surface sensitive techniques were employed in our earlier work on Au_xPd_{1-x} alloy films, electronic/chemical structural trends revealed in that work can be directly compared and contrasted with those in the current study of Cu_xPd_{1-x} alloy films.

All photoelectron measurements were carried out at the 5 m toroidal grating monochromator (5 m-TGM) beamline at the Center for Advanced Microstructures and Devices (CAMD) at Louisiana State University. The beamline was equipped with a photoemission endstation utilizing an Omicron EA125 hemispherical electron energy analyzer with a five-channel detector and dual Mg/Al x-ray source. UPS spectra were collected with a constant pass energy of 10 eV at a photon energy of 85 eV in an ultra-high vacuum with a pressure of 10−10 Torr. UPS spectra were collected in normal emission geometry with a 45° incident angle to the surface normal. All UPS spectra were normalized to a point on the background whose intensity solely emerges from inelastic secondary electrons. The binding energies were referenced with respect to the Fermi level of the Cu sample. The surface of the samples was cleaned with ion sputtering (1 keV, Ne+) for 10 min before photoemission measurements to remove any near-surface contaminants. XPS was conducted on the same sample in the same chamber following the UPS measurement. The XPS spectra were collected in constant pass energy mode with a pass energy of 30 eV. The near-surface composition of the 50 nm alloy films was determined by XPS using CASA software to model the data qualitatively.

Figure 1(d) shows the valence EDOS of pure Cu and Pd metals and alloy films of various compositions. Only the EDOS down to 3 eV binding energy (BE) is shown. While the pure Cu film is characterized by filled 3d band states stretching from 2 to 5 eV BE and, smaller unfilled density of s–p states up to E_F, the Pd film is characterized by a strong, partially filled 4d spectral weight, which increases from 5 eV BE up to E_F. Although both comprise different band structures and spectral weights for their densities of states, it is apparent that the Pd valence bands directly overlap in energy with the Cu *d*-band below 2 eV, akin to the Au_xPd_{1-x} alloy film system. Upon alloying these metals, notable changes in the d-band structure of both Cu and Pd are revealed with UPS. As the Pd content of the alloy increases, the centroid of the *d*-band of Cu moves toward E_F, while the Pd 3d band center shifts away from E_F (toward high BE), see **Figure 1(d)**. Furthermore, accompanying this shift in the Pd *d*-bands with increasing Cu concentration, there is a concomitant attenuation of the Pd density of states at or near E_F (within 0.9 eV). For the 50–50 alloy, there remain appreciable Pd states near E_F, but they rapidly decrease at higher Cu concentrations.

With the knowledge that *d*-states close to the Fermi level are a requisite for NIR applications, the UPS data allow us to directly compare the EDOS as a function of alloy composition. As shown in the shaded region in Figure 1(d), upon alloying Cu with only 4% Pd, the measured EDOS at 0.8 eV (1550 nm) already appreciably increases compared to Cu. Further addition of Pd into the alloy, for example, at 32%, increases the measured photoemission feature by ~eightfold, which is 62% of the value of pure Pd at the same energy.

Electron Dynamics by Ultrafast Pump-Probe Spectroscopy

The change in conductivity was investigated in 5-nm thick Cu_xPd_{1-x} alloys upon 1550 nm excitation using time-resolved terahertz (THz) spectroscopy (TRTS) in transmission geometry. All films were deposited on Z-cut quartz to avoid THz absorption by the substrate. TRTS was performed with a regeneratively amplified Ti:Sapphire laser (Coherent Libra, 800 nm, 1 kHz, 50 fs pulse duration) coupled to a home-built spectrometer. The sample was excited with a 1550 nm pump using an optical parametric amplifier (Coherent TOPAS). Broadband terahertz radiation (0.2–2 THz) was generated and detected using ZnTe nonlinear crystals. The change in transmission upon chopped photoexcitation was normalized by the non-photoexcited signal to determine $\Delta T/T$. More details on the THz setup can be found elsewhere. The 1550 nm pump and THz probe spot size were measured using a translating razor blade by recording the transmitted power as a function of translated distance. An error function was used to extract the pump and probe spot size at the sample position. The pump and probe spot sizes were 3.2 and 2.3 mm in diameter, respectively. For all the THz measurements, the fluence was kept at 90 μJ cm^{-2}.

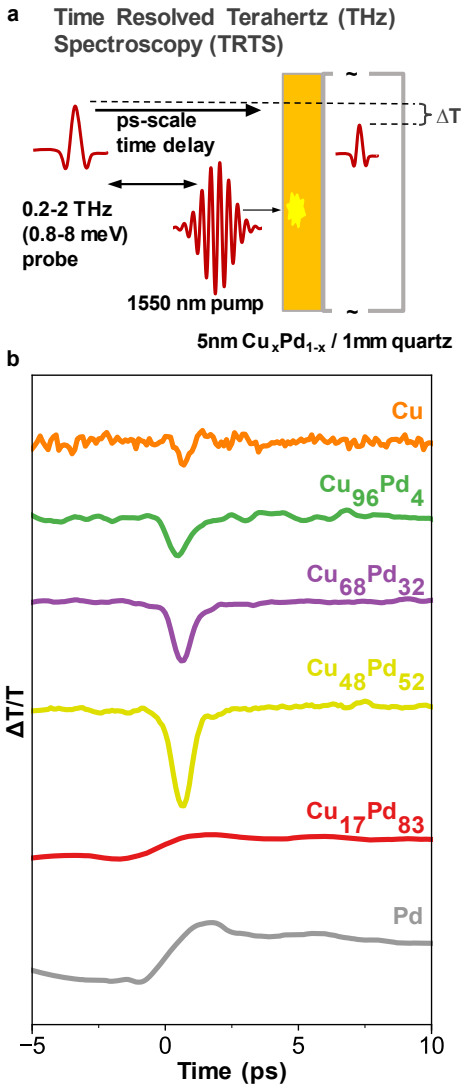

Figure 2. (a) Sketch of TRTS experimental setup. (b) Transient differential transmittance (ΔT/T) of a terahertz probe upon excitation from a 1550 nm pump pulse for pure and alloy films. Positive features such as those in Pd-rich films indicate reduced conductivity after thermalization of hot carriers. Dilute Pd films have negative, picosecond-scale peaks.

We studied the carrier dynamics of 5 nm thick Cu, Pd and Cu_xPd_{1-x} films on Z-cut quartz substrates after a 1550 nm pump by probing the temporal change in broadband terahertz (THz) transmission as shown in Figure 2(a). ΔT/T is the differential peak electric field of the terahertz pulse transmitted through the sample upon photoexcitation, normalized by the peak electric field without photoexcitation. In general, an increase in terahertz transmission corresponds to a decrease in conductivity. Figure 2(b) shows a barely measurable change in ΔT/T upon photoexcitation of pure Cu but a sharp negative peak in ΔT/T at early times for Pd fractions up to ~50 at. %. Alloys beyond 50 at. % Pd display positive contributions to ΔT/T persisting for >5 ps. These positive features are due to thermalization of hot carriers into the lattice. The negligible change in ΔT/T for the pure Cu films is a result of the 1550 nm (~0.8 eV) excitation being below the interband energy threshold of Cu (~2.1 eV). Interestingly, the dilute Pd alloys show a sharp decrease in ΔT/T at early times. We attribute this to an increase in photoconductivity due to the generation of non-thermalized hot carriers. As the Pd fraction in the alloy increases, up to ~50 at. %, the amplitude of the negative dip in ΔT/T at early times also increases. This clearly shows that increasing the Pd fraction in the alloy provides more accessible d-band states for NIR (i.e., 1550 nm) excited interband transitions and is consistent with the composition-dependent trends in the measured EDOS in Figure 1(d). Notably, the diluted Pd alloys do not display a long-lived rise in ΔT/T due to thermalization of hot carriers. More studies are necessary to confirm the precise mechanism for the lack of thermalization in the dilute Pd alloy films.

2. Fabricate Alloy/Si Schottky diode photodetectors.

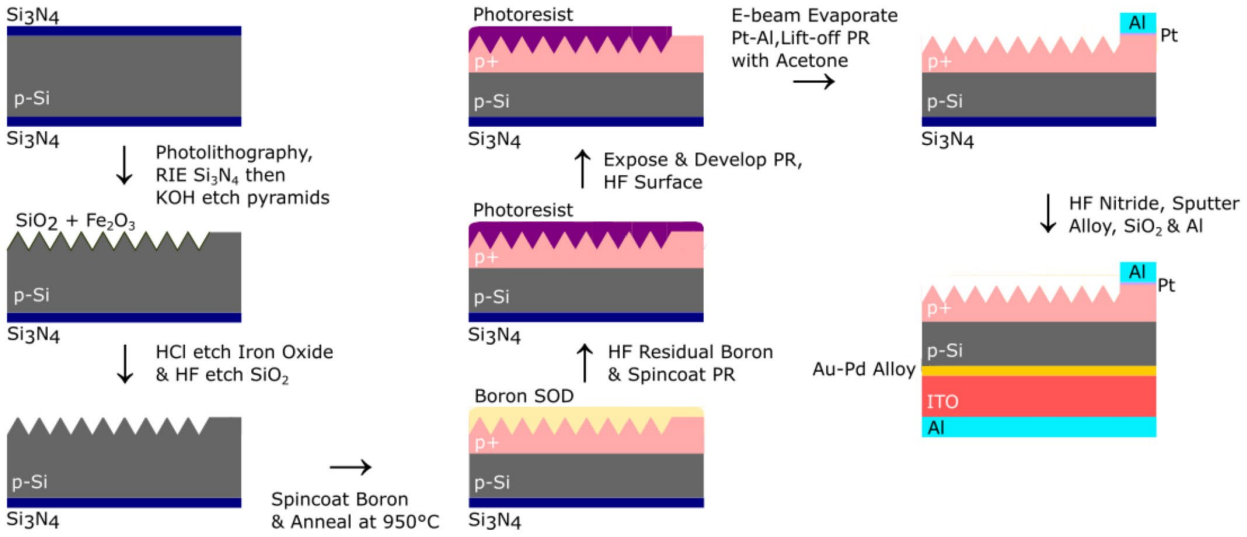

Figure 3. Fabrication flow diagram for the alloy/Si Schottky photodetector

Figure 3 details the steps we used to fabricate preliminary Schottky type devices. We used p-type Si(100)1-10 Ω wafers coated with 50 nm of silicon nitride (Si_3N_4) to protect the back side of the wafer during the top-side fabrication process. KOH surface texturing reduced the Si reflectivity in the infrared from about 33% to around 10%. A spin on boron dopant (Futurrex BDC1-2500) was used to reduce the resistance of the top side of the Si for forming a low resistance ohmic contact to the Al pads.

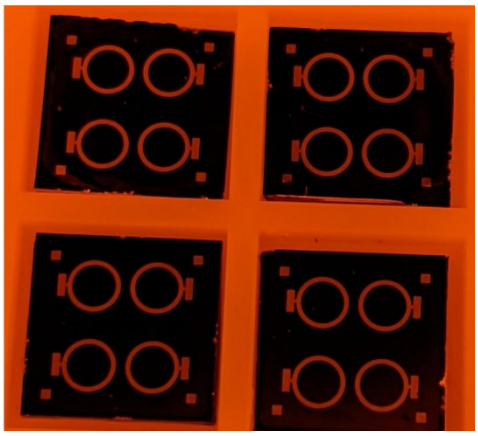

Figure 4. Top side of the prototype SWIR photodetector device

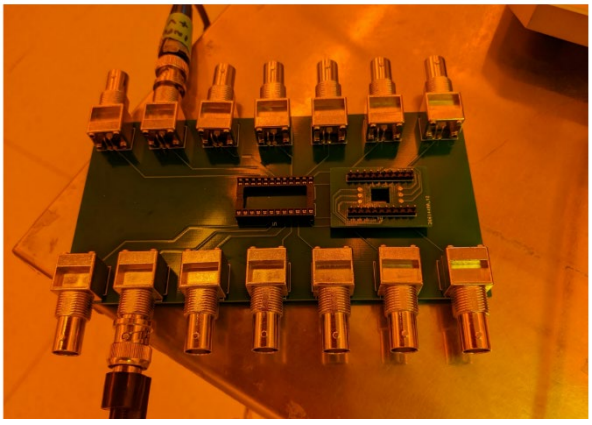

Figure 5. PCB enabling current measurements. Each device contact was bonded to an Al pad on the top and bottom of the small PCB.

3. Characterize the alloy photodetector's responsivity and rise time.

Unfortunately, we were unable to measure responsivity from the devices with 1550 nm excitation. We suspect the issue is due to the design of the contacts, but there could also be issue with the hot-holes being reflected off the alloy/Si interface due to a

mismatch in the momentum. Dark IV curves showed significant series resistance in the device. More work needs to be done to optimize the contacts and the device geometry before we can begin to address the momentum matching issue, which is a known issue in hot-carrier type photodetector devices.

1). Manoukian, G. A.; Kizilkaya, O.; Lendinez, S.; Manuel, L. D. B.; Leite, T. R.; Shirali, K. S.; Shelton, W. A.; Sprunger, P. T.; Baxter, J. B.; McPeak, K. M., Emergent properties from CuPd alloy films under near-infrared excitation. *The Journal of Chemical Physics* **2022,** *157* (17), 174702.
2). Stofela, S. K. F.; Kizilkaya, O.; Diroll, B. T.; Leite, T. R.; Taheri, M. M.; Willis, D. E.; Baxter, J. B.; Shelton, W. A.; Sprunger, P. T.; McPeak, K. M., A Noble-Transition Alloy Excels at Hot-Carrier Generation in the Near Infrared. *Advanced Materials 32* (23), 1906478.