Fabrication and Characterization of Optically Transparent PVDF Films Embedded with Gold Nanoparticles

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Abstract

Polyvinylidene fluoride is a piezoelectric polymer that can be cast into transparent thin films. New properties can be introduced by embedding nanoparticles in this polymer, making it an excellent platform for flexible and tunable electronic and optoelectronic devices. We develop a recipe for embedding plasmonic gold nanoparticles into these films while maintaining their transparency as an initial step to activate optical response in the film. We characterize films made under different poling conditions with and without nanoparticle inclusions using X-ray diffraction. We find that the inclusion of gold nanoparticles screens the poling field and has a sizable effect on the phase of the produced films.

Introduction

Polyvinylidene fluoride (PVDF) is a well-established ferroelectric polymer with highly stable chemical, thermal, mechanical and UV properties.[1–5] Research in recent decades have shown that embedding PVDF with various nanoparticles can enhance its existing properties and potentially promote new functionalities.[1,2,6–8] For example, if a nanoparticle upon optical excitation triggers an intrinsic effect (piezoelectricity or pyroelectricity) in a PVDF thin film to generate a detectable electrical signal, then a new response to optical stimulus is introduced. Such a hybrid system could then be exploited to make flexible and transparent optical sensors in wearable devices. In practice, for such a system to be viable, it is necessary to produce a transparent and ferroelectric PVDF film with the right nanoparticle inclusion. In addition, the density of the particles needs to be substantial enough to produce a measurable effect without affecting the transparency of the film.

In this report, we have taken the initial steps in producing and testing the viability of PVDF films embedded with plasmonic nanoparticles. Plasmonic nanoparticles are well-known for exhibiting size dependent optical resonant properties. At resonance, the optical energy is efficiently absorbed leading to ultra-high enhancement of near-field intensity as well as localized heating.[9] These effects could stimulate the piezoelectric and pyroelectric responses in the PVDF film. While we do not measure for an optical response in the films for this study, we are able to synthesize a transparent PVDF film with plasmonic gold nanoparticles (AuNPs) and confirm that the system exhibits ferroelectricity using X-ray diffraction (XRD). More importantly, we find that the AuNPs have a statistically significant effect on the properties of the PVDF films. This makes the films a promising candidate for further optical studies.

Casting Method

A popular method for creating PVDF structures is the technique of electrospinning. Electrospun plastic sheets have applications in membranes for batteries and electronics.[1–5] However, this method leads to opaque structures. Another method of forming piezoelectric PVDF films is by spin-coating the polymer onto a substrate in the presence of a high electric field.[1] This creates thin PVDF films that are clear and thus allow optical access to the nanoparticles embedded within to activate potential optical properties. This method of producing piezoelectric PVDF devices is cost-effective and relatively straightforward. The

key is to overcome the need for a high electric field utilized to induce a ferroelectric polymer phase (500-700 kV/cm) and to consistently create a ferroelectric film with a high degree of transparency.[10]

Past works have shown that mechanical stress, high annealing temperature, and high electric fields all contribute to encouraging polarized phase formation and transparency during film production.[10–12] Taking these parameters into account, we provide a detailed documentation of a straightforward method for producing transparent PVDF films with and without AuNPs under poled and unpoled conditions. We create multiple films under each condition to facilitate statistical assessment of the consistency of this method and analyze the effect AuNPs and poling have on the final phase composition of the films.

PVDF Film Production

The process for producing bare PVDF thin film is summarized in Figure 1. First, 2 mL of acetone and .25 g of PVDF (in powder form) are mixed in a beaker at 85 °C for ten minutes with a magnetic stirrer. The purpose of the acetone is to suspend and disperse the PVDF powder uniformly in a liquid mixture. This mixture is white and cloudy because PVDF does not dissolve in acetone as shown in Figure 2a. After ten minutes, 1 mL of dimethyl sulfoxide (DMSO) is introduced to the mixture to dissolve the PVDF. The solution is stirred at a temperature of 85 °C for 45 minutes to completely boil off the acetone, leaving only the dissolved PVDF in DMSO. The solution will gradually go from a white and cloudy mixture to a clear and viscous solution during the 45 minutes of mixing as shown in Figure 2b.

After 45 minutes, the solution is ready to be cast. A drop of the solution is placed on a 1cm x 1cm silicon substrate in the spin-coater. The spin-coater chuck is grounded. The solution is spun for 25 seconds at 4,000 rpm. To electrically pole the film, a potential is applied via an aluminum plate placed above the ground plate. We pole our films using either a weaker field at 1.31 kV/cm or a stronger field of 3.25 kV/cm. After spinning, the PVDF coated silicon substrate is transferred to a hot plate and baked for 75 minutes at 85 °C. After baking, the PVDF film is dry enough to be peeled off and stored for XRD measurements.

PVDF-Au Film Production

The 60 nm AuNPs from Sigma Aldrich are suspended in an aqueous solution as shown in Figure 3b. The reddish color is due to the wavelength selective enhanced reflection as a result of the surface plasmon polariton resonance. We find that adding the AuNPs directly to the PVDF and acetone mixture along with the aqueous solution leads to failure in transparent film production. The main reason is that while water cannot dissolve PVDF, PVDF is miscible in DMSO which dissolves PVDF. This combination leads to the formation of a gelatinous substance which is neither transparent nor spreadable into a thin film. To solve this problem, we modify the previous procedure to eliminate the water while keeping the AuNPs.

The process for producing AuNP embedded PVDF thin film is summarized in Figure 3. We start with 1.5 mL of AuNP solution. This amount can vary depending on the desired final concentration of AuNP. The nanoparticle solution is placed in a centrifuge to separate the AuNPs from the water. After centrifuging,

most of the water is removed using a pipet while leaving the AuNPs at the bottom of the test tube. The AuNPs are immediately resuspended in 4 mL of acetone with a vortex mixer to avoid permanent aggregation of the AuNPs which can destroy its plasmonic property.

The 4 mL acetone/AuNP solution is mixed with 0.25 g of PVDF powder in a beaker at 105 °C for 10 minutes. This increased temperature, in contrast to 85 °C in the bare PVDF film production, ensures that any remaining water is boiled off from the mixture. After 10 minutes, 1 mL of DMSO is introduced to the mixture. The solution is stirred continuously at 105 °C for another 50 minutes. As the acetone (and any remaining water) is boiled off, the PVDF dissolves into the DMSO. The solution will go from an opaque, pale pink mixture to a clear, viscous red-pink hue shown in Figure 3c. The fact that this coloration remains is a sign that the plasmonic property of the AuNPs is maintained. At this point, the solution is viscous enough to be cast. The spin coating step is the same as that in the bare film production. After the spin-coating step, the AuNP PVDF film with substrate is placed on a hot plate for 75 minutes at 85 °C and peeled off afterwards to be characterized in XRD. Examples of PVDF films produced without and with AuNPs are presented in Figure 4a and 4b, respectively.

Results

XRD is used to characterize the phase compositions of the PVDF films. We expect to observe peaks associated with the three most common phases in PVDF (α, β, and γ). The non-ferroelectric α phase has two dominant double peaks around 2θ = 18.4° and 19.9°. For the ferroelectric phases, the dominant γ phase peak is at 2θ = 20.2° whereas the dominant β phase peak is at 2θ = 20.8°.[13,14] These peaks are all near each other making it difficult to identify the phases of the films using this group alone. It is then helpful to look at minor peaks at larger angles for more clues on the phase composition of our films. At larger 2θ values, the α phase has a wide, short peak at 26.5°. Similarly, the γ phase has a wide, short peak at 39°. It is often noted that a small peak at 36.3° is associated with the β phase. However, we found it unhelpful for phase identification because there are similarly sized peaks from the α and γ phases nearby.[8,14–16] Nevertheless, we have highlighted this peak in Figure 5 to distinguish it from the others. Using both peak information from small and large 2θ, we then assigned the appropriate phase — or combination of phases — for each film. Figure 5a highlights three examples of pure phase assignments using the guide described above. Figure 5b gives examples of the mixed phase assignments. The α-β mix is assigned to any films whose XRD spectra have a combination of the α phase peaks at 18.4° and 26.5° and a shift of the tallest peak towards 19.9°. The β-γ mix is assigned to any films which exhibited no signs of being in the α phase and with its tallest peak directly in the middle of 20.2° and 20.6°. For example, in Figure 5b we see the β-γ mix has its tallest peak at 20.4°. We note that our assignment of pure phase only means that the particular phase has the majority fraction and does not necessarily mean 100% purity.

The phase categorization results for the 93 successful films produced is presented in Figure 6. The table in Figure 6a provides a summary of the number of films produced under each category. For unpoled films (no field), there is no clear indication of a preferred phase for both films with and without AuNP inclusions, except maybe a small tendency towards the γ phase as seen in Figure 6b. We attribute this to the high annealing temperature during film production which has been observed in previous works to produce ferroelectric films even without a poling field being applied.[11,12] An important point to note is that the AuNPs present no significant effect on the films under the unpoled condition. Conversely, the difference in poled films is apparent as shown in Figure 6c and 6d. Poled films containing no AuNPs are only found in the ferroelectric phases. On the other hand, the poled films embedded with AuNPs exhibit a trend more like that of unpoled films and still support the non-ferroelectric α phase. This difference between films made with and without AuNPs is more apparent at the weaker field of 1.31 kV/cm field as shown in Figure 6c. At this field strength, poling completely removes the α phase from the films without AuNPs but does not do so for films with AuNPs. In the case of the stronger field of 3.25 kV/cm, a pure α phase no longer forms in films with AuNPs. Rather, a combination α-β phase is still found as seen in Figure 6d. This implies that the embedded AuNPs are having a notable effect on the PVDF during the production process. Since these particles are metal, it is likely that they are screening the electric field in their immediate vicinity and hence reducing the poling effect for the PVDF nearby. Even though the introduction of AuNPs is reducing the formation of pure β phase in the films, if the poling field is strong enough, as seen in Figure 6d, the non-ferroelectric α can still be reduced. This result suggests that the quantity of AuNPs present is enough to produce a measurable modification of the PVDF films on a macroscopic scale while still maintaining film transparency. This also means that these hybrid films will be viable for future investigations to explore localized optical modification of PVDF using laser light at the resonant plasmonic frequency of the AuNPs.

Conclusion

We have detailed a straightforward and cost-effective method for synthesizing poled/unpoled optically transparent PVDF films with and without AuNPs. Using XRD, we have characterized our films and find that AuNP inclusion in PVDF has a considerable effect on the phase properties of the film under poling condition. This effect is likely due to the screening effect of the metallic nanoparticles. This result presents a promising outlook for these films as transparent optical sensors and optically tunable optoelectronic devices.

Declarations

Acknowledgement

Competing interests

The authors declare no competing interests.

Data Availability

The datasets generated during and analyzed during the current study are available from the corresponding author on reasonable request.

Author Contributions Statement

All authors contributed to the development of the method for film productions described in this paper. Caleb Duff and Alan Rowland collected all XRD data and analyzed said data. Alex Long designed and constructed the spin-coating and poling system by modifying a centrifuge. All authors reviewed the manuscript.

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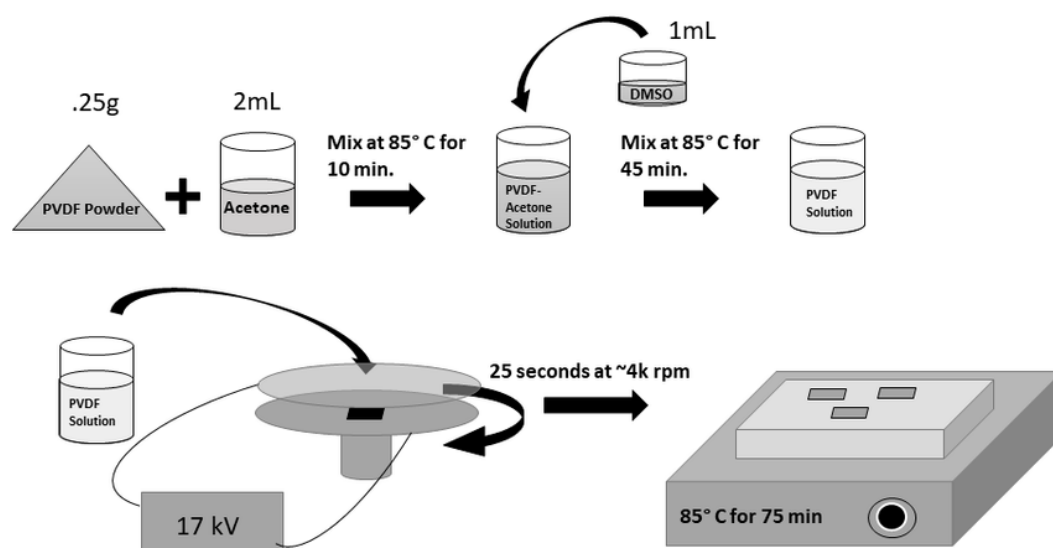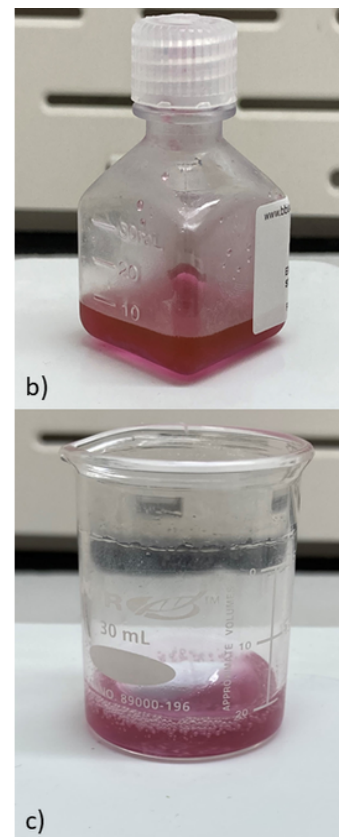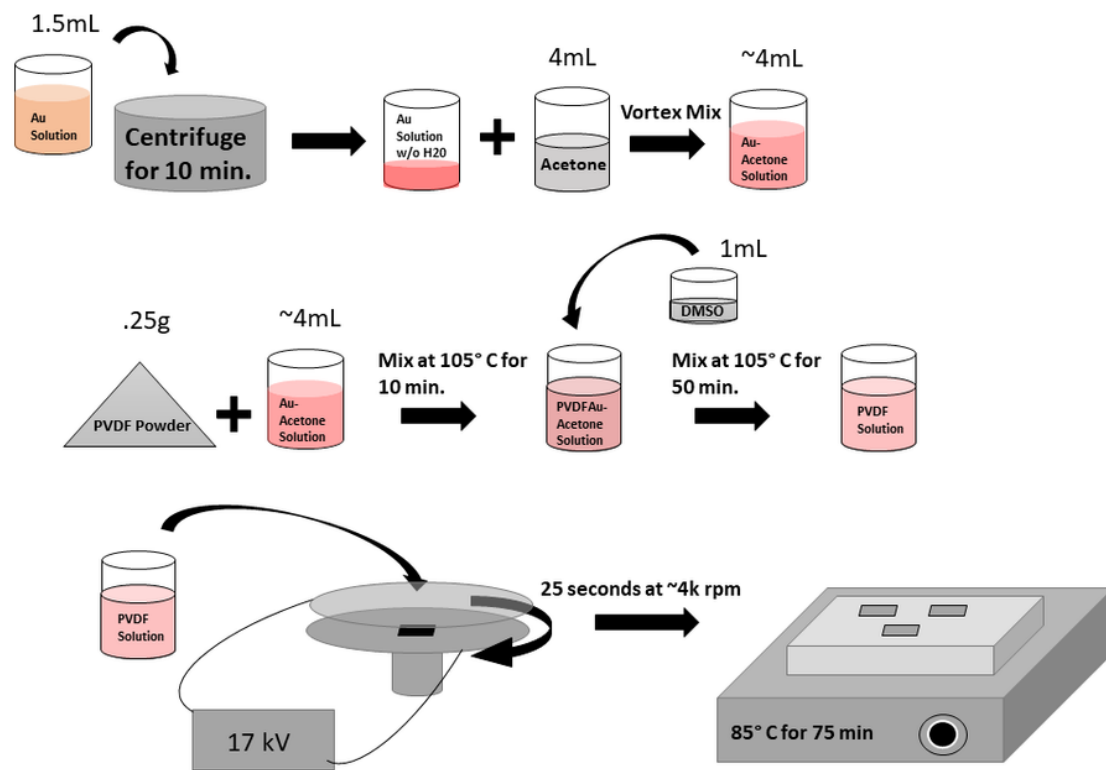
Figures

Figure 1

The method for casting PVDF films with no added AuNP.

Figure 2

PVDF solution before and after putting DMSO into the beaker. Before adding DMSO into the beaker, one can observe bubbles throughout the solution. After adding DMSO, the bubbles are gone and the solution clears up, producing the image on the right.

Figure 3

a) The method for casting PVDF films with AuNP. b) The original solution of AuNP before removing the water and vortex mixing with acetone. c) The solution's appearance while mixing. The deep red, pink hue is from the AuNP. This is what the solution looks like during the mixing process after the DMSO has been added.
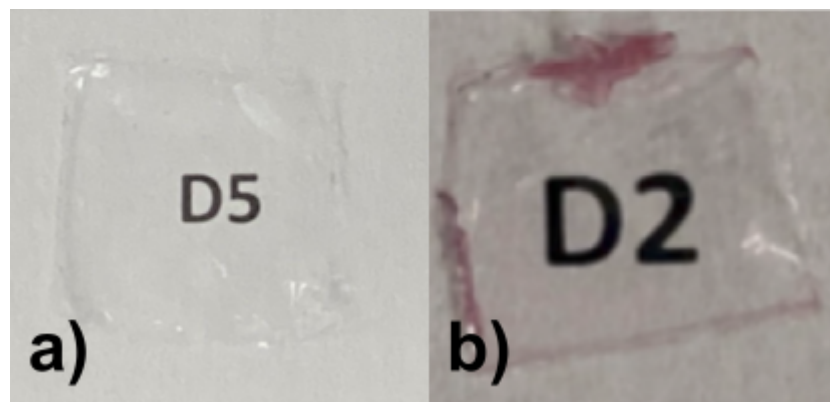

Figure 4

Examples of spin-coated a) bare PVDF film and b) PVDF film embedded with AuNP. Both films are transparent as desired. While the bare film is colorless, the AuNP film retains a pinkish hue indicative of the intact plasmonic property of the 60nm AuNPs.
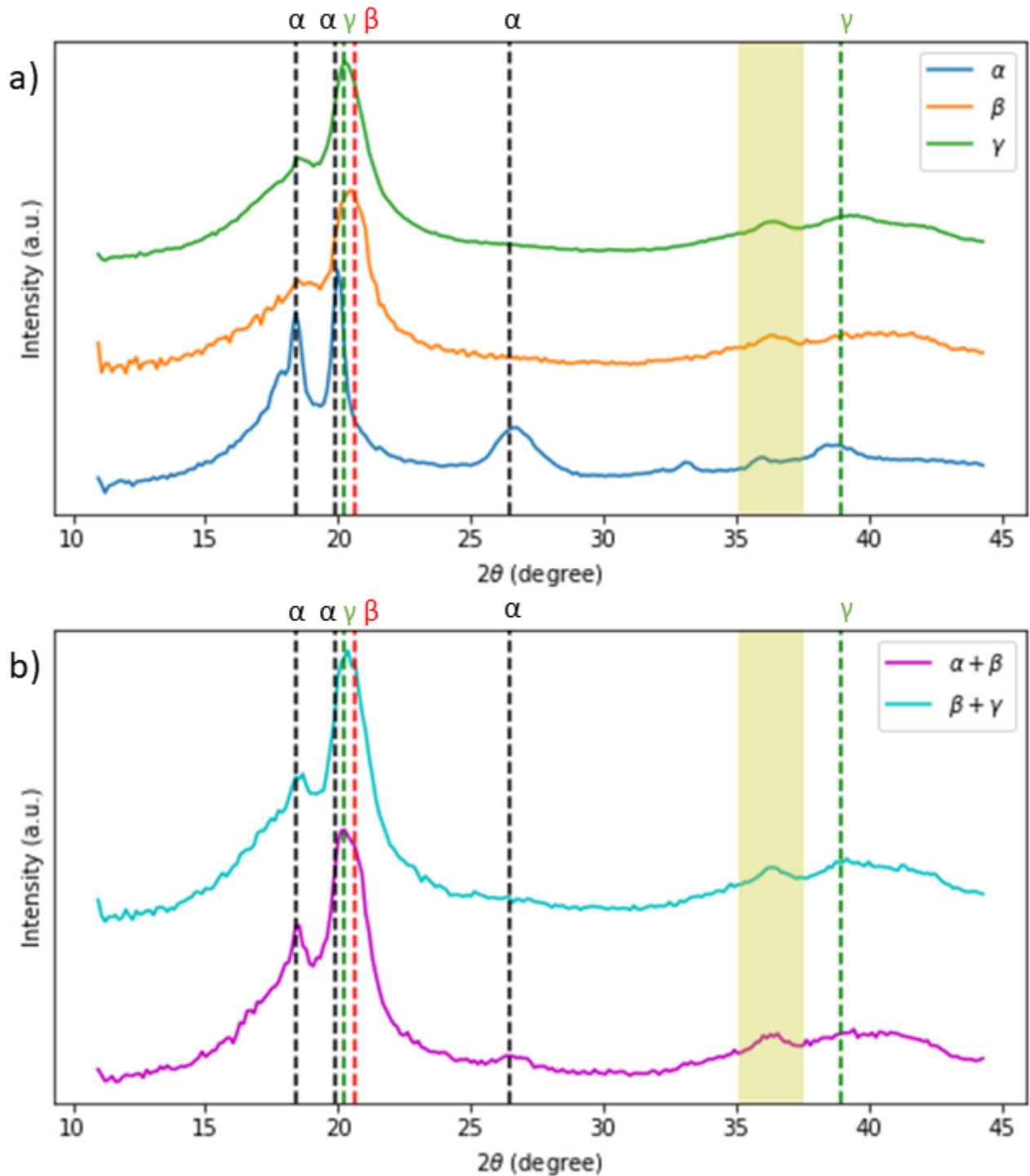
Figure 5

a) Examples of XRD spectra for films with the three pure phase assignments. b) Examples of XRD spectra for films with the two mixed phase assignments. The α-β mix represents films with signatures of both the α and β phases. The β-γ mix represents films whose main peak lay in the middle of 20.2° and 20.6° and show no α features.
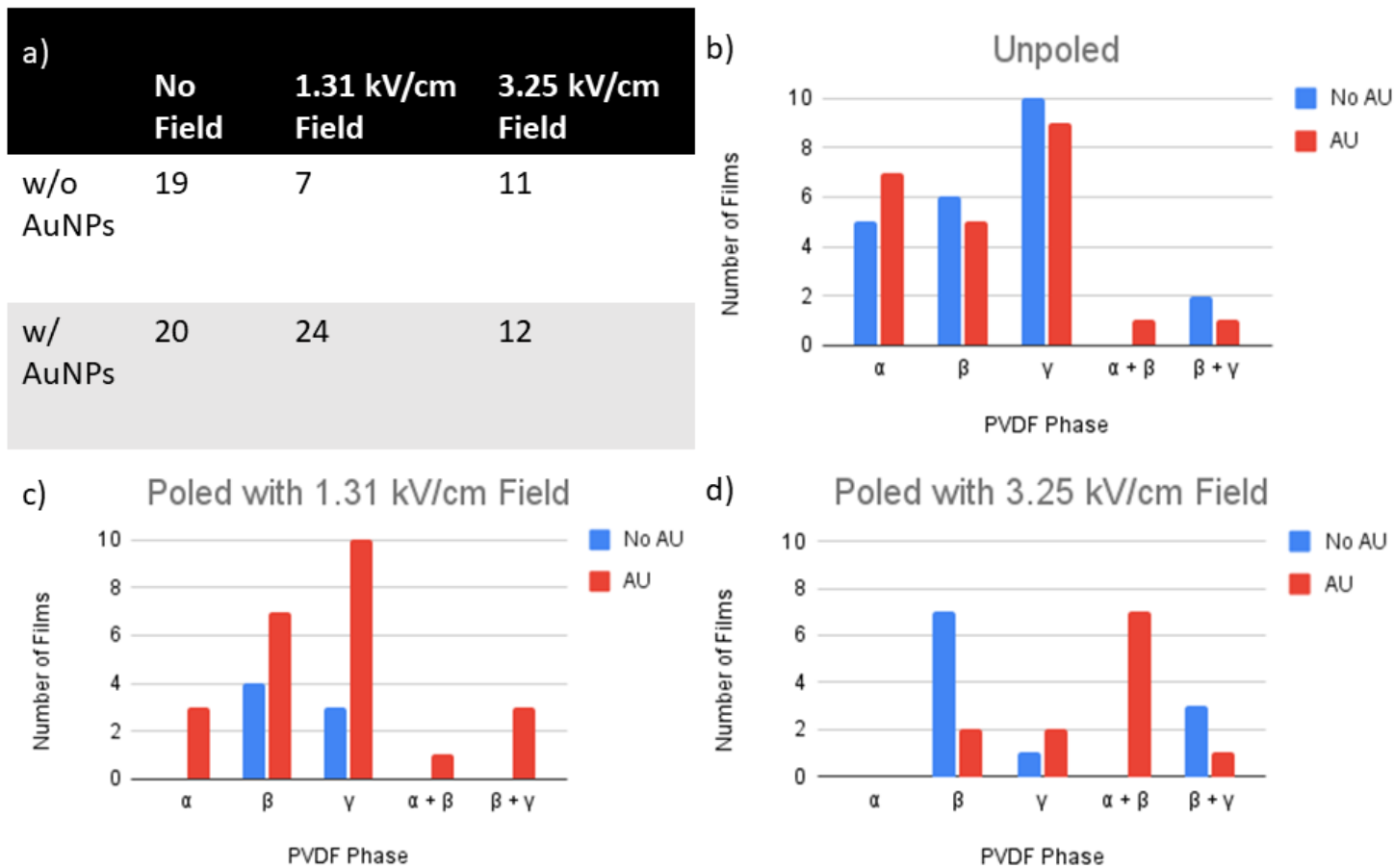
a)

	No Field	1.31 kV/cm Field	3.25 kV/cm Field
w/o AuNPs	19	7	11
w/ AuNPs	20	24	12

b)

Unpoled

c)

Poled with 1.31 kV/cm Field

d)

Poled with 3.25 kV/cm Field

Figure 6

a) A table summary of the numbers of film produced in each category. The different number of films in each category is due to film destruction during removal from the silicon substrates. b-d) Bar graphs detailing the phase composition for a set of films with a specific constraint (i.e., poled, gold-embedded, etc.). b) A comparison of all films made under unpoled condition. c) A comparison of all films poled with a weaker 1.31 kV/cm electric field. d) A comparison of all films poled with a stronger 3.25 kV/cm electric field.