What is claimed is:

1. A method of forming a semiconductor device, the method comprising:

depositing a first metal layer by physical vapor deposition (PVD) on a semiconductor substrate surface with at least one feature formed thereon, the at least one feature having at least one opening having a width, at least one sidewall, and a bottom, the at least one feature extending a feature depth from a top surface to the bottom, the first metal layer forming on the top surface, on the at least one sidewall, and on the bottom;

exposing the semiconductor substrate surface to one or more monomers to form a flowable polymer film on the first metal layer within the at least one feature, the flowable polymer film forming on the first metal layer on the bottom, the one or more monomers selected from one or more of amines with bi-functional groups, aldehydes with bi-functional groups, cyanates with bi-functional groups, ketones with bi-functional groups, and alcohols with bi-functional groups;

selectively removing at least a portion of the first metal layer from the top surface and the at least one sidewall; and

removing the flowable polymer film to expose the first metal layer on the bottom of the at least one feature.

2. The method of claim 1, wherein the first metal layer comprises one or more of tungsten (W), molybdenum (Mo), ruthenium (Ru), cobalt (Co), nickel (Ni), titanium (Ti), and tantalum (Ta).

3. The method of claim 2, wherein the first metal layer formed on the bottom of the at least one feature reacts with the semiconductor substrate surface to form a metal silicide, and wherein the metal silicide comprises one or more of tungsten silicide (WSi_x), ruthenium silicide ($RuSi_x$), nickel silicide ($NiSi_x$), titanium silicide ($TiSi_x$), molybdenum silicide ($MoSi_x$), cobalt silicide ($CoSi_x$), or tantalum silicide ($TaSi_x$).

4. The method of claim 1, further comprising selectively depositing a second metal layer on the first metal layer to fill the at least one feature.

5. The method of claim 4, wherein the second metal layer comprises one or more of tungsten (W), molybdenum (Mo), ruthenium (Ru), cobalt (Co), nickel (Ni), titanium (Ti), or tantalum (Ta).

6. The method of claim 4, wherein the first metal layer and the second metal layer are the same.

7. The method of claim 1, the semiconductor substrate surface is exposed to the one or more monomers at a temperature in a range of from 30 °C to 400 °C.

8. The method of claim 1, wherein the amines have a formula of $H_2N\text{-}(CH_x)_n\text{-}NH_2$, where n is an integer in a range of from 1 to 20 and x is 1 or 2, wherein the aldehydes have a formula of $OHC\text{-}(CH_x)_m\text{-}CHO$, where m is an integer in a range of from 2 to 20 and x is 1 or 2, and wherein the cyanates have a formula of $NCO\text{-}(CH_x)_p\text{-}OCN$, where p is an integer in a range of from 2 to 20 and x is 1 or 2.

9. The method of claim 1, wherein the flowable polymer film has a flexibility suitable for filling the bottom of the at least one feature.

10. The method of claim 1, wherein selectively removing the portion of the first metal layer comprises exposing the semiconductor substrate surface to a fluorine-based plasma or a chlorine-based plasma.

11. The method of claim 1, wherein removing the flowable polymer film comprises exposing the semiconductor substrate surface to one or more of a thermal process or a hydrogen (H_2) plasma treatment.

12. The method of claim 1, comprising repeating the operations of: forming a flowable polymer film on the first metal layer, selectively removing at least a portion of the first metal layer from the top surface and the at least one sidewall, and removing the flowable polymer film.

13. The method of claim 1, wherein the feature depth is in a range of about 5 nm to about 500 nm.

14. The method of claim 1, wherein the polymer has a thickness less than or equal to the feature depth and wherein the thickness is in a range of about 1% to about 99% of the feature depth.

15. A method of forming a semiconductor device, the method comprising:

depositing a first metal layer on a substrate surface with at least one feature formed thereon, the at least one feature including at least one opening, at least one sidewall, and a bottom, the at least one feature extending a feature depth from a top surface to the bottom, the first metal layer forming on the top surface, on the at least one sidewall, and on the bottom;

exposing the substrate surface to one or more monomers to form a flowable polymer film on the first metal layer within the at least one feature, the flowable polymer film forming on the first metal layer on the bottom, the one or more monomers selected from one or more of amines with bi-functional groups, aldehydes with bi-functional groups, cyanates with bi-functional groups, ketones with bi-functional groups, and alcohols with bi-functional groups;

selectively removing the first metal layer from the top surface and from the at least one sidewall;

removing the flowable polymer film to expose the first metal layer on the bottom of the at least one feature; and

selectively depositing a second metal layer on the first metal layer to fill the at least one feature.