Since the plain stress matrix is symmetric, there's a set of eigenvectors, $\bar{v}_1$ and $\bar{v}_2$, which form an orthonormal basis. So for all vector $\bar{n}$, $\bar{n}^{\mathrm{T}}\underline{\underline{\sigma}}\bar{n}$ can be rewritten as

$$\sigma_n = \bar{n}^{\mathrm{T}}\underline{\underline{\sigma}}\bar{n} = (k_1\bar{v}_1 + k_2\bar{v}_1)^{\mathrm{T}}\underline{\underline{\sigma}}(k_1\bar{v}_1 + k_2\bar{v}_2) = k_1^2\lambda_1 + k_2^2\lambda_2 \in [\lambda_2, \lambda_1],$$

where λ_1 and λ_2 are eigenvalues of $\bar{v}_1$ and $\bar{v}_2$ respectively, and $\lambda_1 \geq \lambda_2$. And σ_n reaches its maximum or minimum, if and only if $\bar{n}$ is in the direction of $\bar{v}_1$ or $\bar{v}_2$, respectively, which is equivalent to vanishing of shear stresses.